DIRECTORATE OF EDUCATION Govt. of NCT, Delhi

SUPPORT MATERIAL (2018-2019)

Class: XI

Chemistry

Under the Guidance of

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PREFACE

It gives me immense pleasure to present the Support Material for various subjects. The material prepared for students of classes IX to XII has been conceived and developed by a team comprising of the Subject Experts, Members of the Academic Core Unit and teachers of the Directorate of Education.

The subject wise Support Material is developed for the betterment and enhancement of the academic performance of the students. It will give them an insight into the subject leading to complete understanding. It is hoped that the teachers and students will make optimum use of this material. This will help us achieve academic excellence.

I commend the efforts of the team who have worked with complete dedication to develop this matter well within time. This is another endeavor of the Directorate to give complete support to the learners all over Delhi.

Sanjay Goel, IAS



Director

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Date: 8/8/2018

D.O. No. PS/DE/2018/343

DIRECTOR'S MESSAGE

Dear Students,

Through this Support Material, I am getting an opportunity to communicate directly with you and I want to take full advantage of this opportunity.

In Delhi, there are approximately 1020 other government schools like yours, which are run by Directorate of Education. The Head Quarters of Directorate of Education is situated at Old Secretariat, Delhi-54.

All the teachers in your school and officers in the Directorate work day and night so that the standard of our govt. schools may be uplifted and the teachers may adopt new methods and techniques to teach in order to ensure a bright future for the students.

Dear students, the book in your hand is also one such initiative of your Directorate. This material has been prepared specially for you by the subject experts. A huge amount of money and time has been spent to prepare this material. Moreover, every year, this material is reviewed and updated as per the CBSE syllabus so that the students can be updated for the annual examination.

Last, but not the least, this is the perfect time for you to build the foundation of your future. I have full faith in you and the capabilities of your teachers. Please make the fullest and best use of this Support Material.

DIRECTOR (EDUCATION)

Dr. (Mrs.) Saroj Bala Sain Addl. Director of Edn. (School)/Exam



Govt. of NCT of Delhi Directorate of Education Old Secretariat, Delhi-110054 Tel.: 23890023

> D.O. No. PA/Add. DECSON) 80 Date: 16/07/2018

It gives me immense pleasure and a sense of satisfaction to forward the support material for classes IX to XII in all subjects. The support material is continuously revised redesigned and updated by a team of subject experts, members of Core Academic Unit and teachers from various schools of DOE.

Consistent use of support material by the students and teachers will make the year long journey seemless and enjoyable. The purpose of providing support material has always been to make available ready to use material which is matchless and most appropriate.

My commendation for all the team members for their valuable contribution.

Dr. Saroj Bala Sain Addl.DE (School)

DIRECTORATE OF EDUCATION Govt. of NCT, Delhi

SUPPORT MATERIAL (2018-2019)

Chemistry
Class: XI
(English Medium)

NOT FOR SALE

PUBLISHED BY: DELHI BUREAU OF TEXTBOOKS

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Course Structure

Class : XI (Theory) (2018-19) Chemistry

Total period (Theory 160 + Practical 60)

Time: 3 Hours] Total Marks: 70

Unit No.	Title	No. of Periods	Marks
Unit I	Some Basic Concepts of Chemistry	08	
Unit II	Structure of Atom	10	08
Unit III	Classification of Elements and	06	04
	Periodicity in Properties		
Unit IV	Chemical Bonding and Molecular	14	
	Structure		
Unit V	States of Matter: Gases and Liquids solid	s 18	
Unit VI	Chemical Thermodynamics	16	20
Unit VII	Equilibrium	14	
Unit VIII	Redox Reactions	06	
Unit IX	Hydrogen	08	20
Unit X	s -Block Elements	10	
Unit XI	p -Block Elements	18	
Unit XII	Organic Chemistry: Some Basic	14	
	Principles and Techniques		
Unit XIII	Hydrocarbons	12	18
Unit XIV	Environmental Chemistry	06	
	Total	160	70

Unit I: Some Basic Concepts of Chemistry

8 Periods

General Introduction: Importance and scope of chemistry.

Nature of matter, laws of chemical combination, Dalton's atomic theory: concept of elements, atoms and molecules.

Atomic and molecular masses, mole concept and molar mass, percentage composition, empirical and molecular formula, chemical reactions, stoichiometry and calculations based on stoichiometry.

Unit II: Structure of Atom

10 Periods

Bohr's model and its limitations, concept of shells and subshells, dual nature of matter and light, de Broglie's relationship, Heisenberg uncertainty principle, concept of orbitals, quantum numbers, shapes of s, p and d orbitals, rules for filling electrons in orbitals - Aufbau principle, Pauli's exclusion principle and Hund's rule, electronic configuration of atoms, stability of half-filled and completely filled orbitals.

Unit III: Classification of Elements and Periodicity in Properties

06 Periods

Modern periodic law and the present form of periodic table, periodic trends in properties of elements -atomic radii, ionic radii, inert gas radii, Ionization enthalpy, electron gain enthalpy, electronegativity, valency. Nomenclature of elements with atomic number greater than 100

Unit IV: Chemical Bonding and Molecular Structure 14 Periods

Valence electrons, ionic bond, covalent bond, bond parameters, Lewis structure, polar character of covalent bond, covalent character of ionic bond, valence bond theory, resonance, geometry of covalent molecules, VSEPR theory, concept of hybridization, involving s, p and d orbitals and shapes of some simple molecules, molecular orbital theory of homonuclear diatomic molecules(qualitative idea only), hydrogen bond.

Unit V: States of Matter: Gases, Liquids and Solids 18 Period

Three states of matter, intermolecular interactions, types of bonding, melting and boiling points, role of gas laws in elucidating the concept of the molecule, Boyle's law, Charles law, Gay Lussac's law, Avogadro's law, ideal behaviour, empirical derivation of gas equation,



Avogadro's number, ideal gas equation. Deviation from ideal behaviour, liquefaction of gases, critical temperature, kinetic energy and molecular speeds (elementary idea)

Liquid State: vapour pressure, viscosity and surface tension (qualitative idea only, no mathematical derivations)

Solid state: Classification of solids based on different binding forces: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea). Unit cell in two dimensional and three dimensional lattices, calculation of density of unit cell, packing in solids, packing efficiency, voids, number of atoms per unit cell in a cubic unit cell, point defects, electrical and magnetic properties.

Unit VI: Chemical Thermodynamics

16 Periods

Concepts of System and types of systems, surroundings, work, heat, energy, extensive and intensive properties, state functions. First law of thermodynamics -internal energy and enthalpy, heat capacity and specific heat, measurement of ΔU and ΔH , Hess's law of constant heat summation, enthalpy of bond dissociation, combustion, formation, atomization, sublimation, phase transition, ionization, solution and dilution. Second law of Thermodynamics (brief introduction). Introduction of entropy as a state function, Gibb's energy change for spontaneous and non-spontaneous processes, criteria for equilibrium. Third law of thermodynamics (brief introduction).

Unit VII: Equilibrium

14 Periods

Equilibrium in physical and chemical processes, dynamic nature of equilibrium, law of mass action, equilibrium constant, factors affecting equilibrium- Le Chatelier's principle, ionic equilibrium- ionization of acids and bases, strong and weak electrolytes, degree of ionization, ionization of poly basic acids, acid strength, concept of pH, Henderson Equation, hydrolysis of salts (elementary idea), buffer solution, solubility product, common ion effect (with illustrative examples).

Unit VIII: Redox Reactions

06 Periods

Concept of oxidation and reduction, redox reactions, oxidation number, balancing redox reactions, in terms of loss and gain of electrons and change in oxidation number, applications of redox reactions.



Unit IX: Hydrogen

08 Periods

Position of hydrogen in periodic table, occurrence, isotopes, preparation, properties and uses of hydrogen, hydrides-ionic covalent and interstitial; physical and chemical properties of water, heavy water, hydrogen peroxide -preparation, reactions and structure and use; hydrogen as a fuel.

Unit X: s-Block Elements (Alkali and Alkaline Earth Metals) 10 Periods

Group 1 and Group 2 Elements General introduction, electronic configuration, occurrence, anomalous properties of the first element of each group, diagonal relationship, trends in the variation of properties (such as ionization enthalpy, atomic and ionic radii), trends in chemical reactivity with oxygen, water, hydrogen and halogens, uses. Preparation and Properties of Some Important Compounds: Sodium Carbonate, Sodium Chloride, Sodium Hydroxide and Sodium Hydrogencarbonate, Biological importance of Sodium and Potassium. Calcium Oxide and Calcium Carbonate and their industrial uses, biological importance of Magnesium and Calcium

Unit XI: p-Block Elements

18 Periods

General Introduction to *p***-Block Elements :**

Group 13 Elements: General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous properties of first element of the group, Boron-physical and chemical properties, some important compounds, Borax, Boric acid, Boron Hydrides, Aluminium: Reactions with acids and alkalies, uses.

Group 14 Elements : General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous behaviour of first elements. Carbon-catenation, allotropic forms, physical and chemical properties; uses of some important compounds: oxides. Important compounds of Silicon and a few uses: Silicon Tetrachloride, Silicones, Silicates and Zeolites, their uses.

Group 15 Elements : General introduction, electronic configuration, occurrence, oxidation states, trends in physical and chemical properties; Nitrogen preparation properties and uses; compounds of Nitrogen, preparation and properties of Ammonia and Nitric Acid, Oxides of



Nitrogen(Structure only); Phosphorus - allotropic forms, compounds of Phosphorus: Preparation and Properties of Phosphine, Halides and Oxoacids (elementary idea only).

Unit XII: Organic Chemistry -Some Basic Principles and Technique 14 Periods

General introduction, methods of purification, qualitative and quantitative analysis, classification and IUPAC nomenclature of organic compounds. Electronic displacements in a covalent bond: inductive effect, electromeric effect, resonance and hyper conjugation. Homolytic and heterolytic fission of a covalent bond: free radicals, carbocations, carbanions, electrophiles and nucleophiles, types of organic reactions.

Unit XIII: Hydrocarbons

12 Periods

Classification of Hydrocarbons Aliphatic Hydrocarbons:

Alkanes - Nomenclature, isomerism, conformation (ethane only), physical properties, chemical reactions including free radical mechanism of halogenation, combustion and pyrolysis.

Alkenes - Nomenclature, structure of double bond (ethene), geometrical isomerism, physical properties, methods of preparation, chemical reactions: addition of hydrogen, halogen, water, hydrogen halides (Markownikov's addition and peroxide effect), ozonolysis, oxidation, mechanism of electrophilic addition.

Alkynes - Nomenclature, structure of triple bond (ethyne), physical properties, methods of preparation, chemical reactions: acidic character of alkynes, addition reaction of - hydrogen, halogens, hydrogen halides and water.

Aromatic Hydrocarbons: Introduction, IUPAC nomenclature, benzene: resonance, aromaticity, chemical properties: mechanism of electrophilic substitution. Nitration, sulphonation, halogenation, Friedel Craft's alkylation and acylation, directive influence of functional group in monosubstituted benzene. Carcinogenicity and toxicity.

Unit XIV: Environmental Chemistry

06 Periods

Environmental pollution - air, water and soil pollution, chemical reactions in atmosphere, smog, major atmospheric pollutants, acid rain, ozone and its reactions, effects of depletion of ozone layer, greenhouse effect and global warming- pollution due to industrial wastes, green chemistry as an alternative tool for reducing pollution, strategies for control of environmental pollution.



PRACTICALS

Evaluation Scheme for Examination	Marks
Volumetric Analysis	08
Salt Analysis	08
Content Based Experiment	06
Project Work	04
Class record and viva	04
Total	30

PRACTICAL SYLLABUS

Total Periods 60

Micro-chemical methods are available for several of teh practical experiments. Wherever possible such techniques should be used:

A. Basic Laboratory Techniques

- 1. Cutting glass tube and glass rod
- 2. Bending a glass tube
- 3. Drawing out a glass jet
- 4. Boring a cork

B. Characterization and Purification of Chemical Substances

- 1. Determination of melting point of an organic compound.
- 2. Determination of boiling point of an organic compound
- 3. Crystallization of impure sample of any one of the following: Alum, Copper Sulphate, Benzoic Acid.

C. Experiments based on pH

- (a) Any one of the following experiments:
 - Determination of pH of some solutions obtained from fruit juices, solution of known and varied concentrations of acids, bases and salts using pH paper or universal indicator.
 - Comparing the pH of solutions of strong and weak acids of same concentration.
 - Study the pH change in the titration of a strong base using universal indicator.
- (b) Study the pH change by common-ion in case of weak acid and weak bases.

D. Chemical Equilibrium.



CHEMISTRY (Code No. 043)

Question Paper Design

Class-XI (2018-19)

Time: 3 Hours Max. Marks: 70

S. No.	Typology of Questions	Very short Answer (VSA) (1 marks)	Short Answer-I (SA–I) (2 marks)	Short Answer-II (SA-II) (3 marks)	Long Answer (LA) (5 marks)	Total Marks	% Weightage
1.	Remembering—(Knowedge based Simple recall ques- tions, to know specific facts, terms, concepts, prin-ciples, or theories, Identify, define, or recite, information)	2	1	1	-	7	10%
2.	Understanding-(Com- prehension-To be famil- iar with meaning and to understand conceptually, interpret,compare,contrast, explain, paraphrase infor- mation)	-	2	4	1	21	30%
3.	Application (Use abstract information in concrete situation, to apply knowledge to new situations, Use given content to interpret a situation, provide an example, or solve a problem)	-	2	4	1	21	30%
4.	High Order Thinking Skills (Analysis & Syn- thesis-Classify, Compare, Contrast, or differentiate between different pieces of information, Organize and/or integrate unique pieces of information from a variety of sources)	2	-	1	1	10	14%
5.	Evaluation—(Appraise, judge, and/or justify the value or worth of a decision or outcome,or to predict outcomes based on values)	1	2	2	-	11	16%
	TOTAL	5×1=5	7×2=14	12×3=36	3×5=15	70(27)	100%



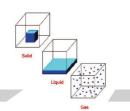
Question Wise Break Up

Type of Ques.	Mark per Ques.	Total No. of Ques.	Total Marks
VSA	1	5	05
SA-I	2	7	14
SA-II	3	12	36
LA	5	3	15
Total		27	70

- 1. Internal Choice: There is no overall choice in the paper. However, there is an internal choice in one question of 2 marks weightage, one question of 3 marks weightage and all the three questions of 5 marks weightage.
- 2. The above template is only a sample. Suitable internal variations may be made for generating similar templates keeping the overall weightage to different form of questions and typology of questions same.

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Chapter - 1

Some Basic Concepts Of Chemistry

- Matter: Anything that has mass and occupy space.
- **Precision :** If refers to the closeness of various measurements for the same quantity.
- **Accuracy:** It refers to the agreement of a particular value to the true value of the result.
- Mass and weight: Mass of a substance is the amount of matter present in body, while weight is the force exerted by gravity on an object. The mass of a substance is constant whereas its weight may vary from one place to another due to change in gravity.
- **Volume :** $1 L = 1 dm^3 = 10^3 cm^3 = 10^{-3} m^3$
- **Temperature :** $K = {}^{\circ}C + 273.15; \frac{{}^{\circ}F 32}{9} = \frac{{}^{\circ}C}{5}$
- **Standard Temperature Pressure (STP) :** 0°C (273.15 K) temperature and 1 atm pressure.
- **Normal Temperature Pressure (NTP) :** 20°C (293.15 K) temperature and 1 atm pressure.
- Standard Ambient Temperature Pressure (SATP): 25°C (298.15 K) temperature and 1 atm pressure
- Scientific Notation: Expressing a number in the form $N \times 10^n$, and N can vary between 1 to 9.99.
- **Significant figures :** These are meaningful digits which are known with certainty.
- Laws of Chemical Combination :
 - Law of Conservation of Mass (Antonie Lavoisier): Mass can neither be created nor be destroyed.
 - ➤ Law of Definite Proportions (Joseph Proust) : A given compound

always contains the same elements in the same proportion by mass.

- ➤ Law of Multiple Proportions (John Dalton): When two elements combine to form two or more compounds, then the different masses of one element, which combine with a fixed mass of the other, bear a simple ratio to one another.
- ➤ Gay Lussac's Law: When gases combine or are produced in a chemical reaction, they do so in a simple ratio provided all gases are in the same temperature and pressure.

e.g.,
$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

2 Vol 1 Vol 2 Vol
(at same T, P)

Atomic Mass: It is defined as the average relative mass of an atom of an element as compared to the mass of an atom of carbon – 12 taken as 12.
 Atomic mass is represented by 'u' (unified mass).

$$1u = 1.66056 \times 10^{-24} \,\mathrm{g}$$

• **Molecular mass**: It is algebraic the sum of the atomic mass of the elements present in the molecule.

For example: Molecular mass of
$$CH_4 = (1 \times 12) + (4 \times 1) = 16 \text{ u}$$

• Avogadro Number: It is the amount of atoms or molecules present in one mole of a substance.

Avogadro number (
$$N_A$$
) = $6.022 \times 10^{23} \text{ mol}^{-1}$

• **Molar Mass**: The mass of one mole of a substance in grams is called its molar mass.

For example : Molar mass of
$$CH_4 = (1 \times 12) + (4 \times 1) = 16g \text{ mol}^{-1}$$

• Mole (n): It is amount of a substance that contains as many particles or entities as the number of atoms in exactly 12 grams of pure C-12.

1 mole of a substance = Molar mass of substance = Avogadro's Number of chemical units = 22.4L volume at STP of gaseous substance

e.g., 1 mole of $\mathrm{CH_4} = 16\mathrm{g}$ of $\mathrm{CH_4} = 6.022 \times 10^{23}$ molecules of $\mathrm{CH_4} = 22.4\mathrm{L}$ at STP

$$n = \frac{wg}{M_m} = \frac{V L(at STP)}{22.4L} = \frac{x \text{ particles}}{N_A} = \frac{MV}{1000}$$

• Molar Volume (V_m) : It is volume occupied by one mole of gas at STP. Molar volume of a gas = 22.4L at STP (273 K, 1atm) or 22.7L at STP (273 K, 1 bar)

Calculating Molar Volume: PV = nRT

:. V =
$$\frac{nRT}{P} = \frac{1\text{mol} \times 0.082\text{L atm K}^{-1}\text{mol}^{-1} \times 273\text{K}}{1 \text{ atm}} = 22.4\text{L}$$

Or

$$V = \frac{nRT}{P} = \frac{1 \text{ mol} \times 0.083 \text{ L bar } \text{K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}}{1 \text{ bar}} = 22.7 \text{ L}$$

• Percentage Composition: Mass % of the element

$$= \frac{\text{Mass of element in a molecule of the compound} \times 100}{\text{Molecular mass of the compound}}$$

- **Empirical Formula :** It represents the simplest whole number ratio of various atoms present in a compound. For *e.g.*, CH is the empirical formula of benzene.
- **Molecular Formula**: It shows the exact number of different of atoms present in a molecule of a compound. For *e.g.*, C₆H₆ is the molecular formula of benzene.
- Relationship between empirical and molecular formulae : Molecular formula = $n \times \text{Empirical formula}$

Where;
$$n = \frac{\text{Molar mass}}{\text{Empirical formula mass}}$$

• Information Conveyed by a chemical equation :

- **Limiting Reagent**: It is the reactant which gets consumed first or limits the amount of product formed.
- Mass Percent: It is the mass of the solute in grams per 100 grams of the solution.

Mass percent=
$$\frac{\text{Mass of solute in } g \times 100}{\text{Mass of solution in } g}$$

• Parts per million (ppm): It is part of solute per million part of solution by mass.

$$ppm = \frac{Parts \text{ of solute (by mass)} \times 10^6}{Parts \text{ of solution (by mass)}}$$

• Molarity (M): It is number of moles of solute dissolved per litre (dm³) of the solution.

Molarity =
$$\frac{\text{No. of moles of solute}}{\text{Volume of solution in L}}$$

Molarity equation :
$$M_1V_1 = M_2V_2$$

(Before dilution) (After Dilution)

Molarity of a solution decreases on increasing temperature.

Molarity of pure water is 55.56 mol L⁻¹

• Molality (m)—It is number of moles of solute dissolved per 1000g (1kg) of solvent.

Molality =
$$\frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$

Molality is independent of temperature.

• **Mole Fraction**(*x*) is the ratio of number of moles of one component to the total number of moles (solute and solvents) present in the solution.

$$x_1 = \frac{n_1}{n_1 + n_2}$$
 and $x_2 = \frac{n_2}{n_1 + n_2}$

The sum of all the mole fractions in a solution is equal to one. i.e., $x_1 + x_2 = 1$

1 - Mark Questions

- 1. Name two chemical compounds used in treatment of cancer.
- 2. What is AZT? Mention its use in medical science.
- **3.** Give an example each of homogeneous and heterogeneous mixture.
- 4. Differentiate solids, liquids & gases in terms of volume & shapes.
- 5. Classify following as pure substances and mixtures: air, glucose, gold, sodium and milk.

- **6.** What is the difference between molecules and compounds? Give examples of each.
- 7. What is the SI unit of density?
- **8.** What is the SI unit of molarity?
- **9.** Define accuracy.
- **10.** What are the two different system of measurement?
- 11. What is the difference between mass & weight?
- **12.** Define significant figures.
- **13.** Define precision.
- **14.** Which measurement is more precise 4.0g or 4.00g? [Ans. 4.00 g]
- 15. How many significant figures are there in (i) 3.070 and (ii) 0.0025?

[**Ans.** (i) 4 (ii) 2]

- **16.** Express the following in the scientific notation : (i) 0.0048 (ii) 234,000
- 17. State Avogadro's law.
- **18.** State law of definite proportions.
- 19. State Gay Lussac's Law of combining volumes of gases.
- 20. If ten volumes of dihydrogen gas react with five volumes of dioxygen gas, how much volume of water vapour would be produced?

 [Ans. 10 volumes]
- 21. Define unified mass (u).
- **22.** Calculate the number of atoms in 32.0 u of He. [Ans. 8]
- 23. Define molar volume of a gas.
- **24.** What is the volume of 17 g of NH_3 gas at STP (298 K, 1 atm) ? [Ans. 22.4 L]
- 25. What is the value of one mole?
- **26.** Calculate the number of molecules present in 22.0 g of CO_2 .

[Ans. 3.011×10^{23}]

27. How many molecules of SO₂ are present in 11.2 L at STP?

[Ans.
$$3.011 \times 10^{23}$$
]

- 28. Which has more number of atoms ? 1.0 g Na or 1.0 g Mg. [Ans. 1.0 g Na]
- **29.** How many oxygen atoms are present in 16 g of ozone (O_3) ?

[Ans.
$$2.007 \times 10^{23}$$
]

30. At STP, what will be the volume of 6.022×10^{23} molecules of H₂?

31. 1L of a gas at STP weighs 1.97g. What is molecular mass?

[Ans.
$$44.128 \text{ g mol}^{-1}$$
]

- 32. Write the relationship between empirical formula and molecular formula.
- **33.** Which is more informative? Empirical formula or Molecular formula.
- **34.** A subtance has molecular formula $C_6H_{12}O_6$ What is its empirical formula.
- **35.** Empirical formula of a compound $X(Molar mass = 78 mol^{-1})$ is CH. Write its molecular formula.
- **36.** How are 0.5 mol Na₂CO₃ and 0.5 M Na₂CO₃ different from each other?
- **37.** Why molality is preferred over molarity of a solution?
- **38.** Define molarity of a solution.
- **39.** What is the effect of temperature on molarity of solution?
- **40.** What is limiting reactant in a reaction?

2 - Mark Questions

- 1. How can we say that sugar is solid and water is liquid?
- 2. How is matter classified at macroscopic level?
- **3.** Classify following substances as element, compounds and mixtures: water, tea, silver, steel, carbon dioxide and platinum.
- **4.** The body temperature of a normal healthy person is 37°C. Calculate its value in °F.

- **5.** At what temperature will both the Celsius and Fahrenheit scales read the same value?
- 6. Convert 5L into m³.
- 7. What does the following prefixes stand for:
 - (a) pico (b) nano (c) micro (d) deci
- **8.** How many significant figures are present in the answer of the following calculations:
 - (i) 0.0125 + 0.8250 + 0.025

(ii)
$$\frac{0.025 \times 298.15 \times .1155}{0.5785}$$

9. Convert '450 pm' into SI unit and write the answer in scientific notation upto 2 significant figures.

[Ans.
$$4.5 \times 10^{-10}$$
 m]

10. The density of vanadium is 5.96 g cm⁻³. Express this in SI unit.

[Ans.
$$5960 \text{ kg m}^{-3}$$
]

- 11. 45.4 L of dinitrogen reacted with 22.7 L of dioxygen and 45.4 L of nitrous oxide was formed. The reaction is given below: 2 N₂ (g)+O₂ (g) → 2 N₂O (g) Which law is being obeyed in this experiment? Write the statement of the law.
- 12. Write main points of Dalton's atomic theory.
- **13.** Give one example each of a molecule in which empirical formula and molecular formula is (i) Same (ii) Different.
- **14.** Calculate the number of moles in the following masses:
 - (i) 7.85g of Fe; (ii) 7.9mg of Ca
- 15. Calculate average atomic mass of chlorine using following data:

Isotope	% Natural abundance	Molar mass		
³⁵ C1	75.77	34.9689		
³⁷ C1	24.33	36.9659	[Ans. 35.5 u]	

- **16.** Calculate the percent of carbon, hydrogen and oxygen in ethanol (C_2H_5OH) [Ans. 52.14%, 13.13%, 34.73%]
- 17. How much copper can be obtained from 100 g of CuSO₄?[Ans. 39.8g]
- **18.** Calculate the amount of water (*g*) produced by the combustion of 16 g of methane. [Ans. 36g]
- **19.** How many moles of methane are required to produce 22 g CO₂ (g) after combustion? [Ans. 0.5 mol]
- **20.** A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass per cent of the solute. [Ans. 10%]
- 21. Calculate molarity of water if its density is 1.00 g mL⁻¹. [Ans. 55.56 M]
- 22. Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution. [Ans. 0.4 M]
- **23.** The density of 3 M solution of NaCl is 1.25 g mL⁻¹. Calculate molality of the solution. [Ans. 2.8m]
- **24.** Calculate the molarity of a solution of ethanol in water in which the mole fraction of ethanol is 0.040 (assume the density of water to be one).

[Ans. 2.31 M]

25. NH_3 gas can be prepared by Haber's process as, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. At a particular moment concentration of all the species is 2 moles; calculate the concentration of N_2 and H_2 taken initially.

[Ans. 3 mole, 5 moles]

- **26.** A sample of drinking water was found to be severely contaminated with chloroform, CHCl₃, supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass).
 - (i) Express this in percent by mass.
 - (ii) Determine the molality of chloroform in the water sample.

[Ans. (i)
$$\sim 15 \times 10^{-14} \text{ g (ii) } 1.25 \times 10^{-4} \text{ m}$$
]

27. Potassium superoxide, KO₂ is used in rebreathing gas masks to generate oxygen.

$$4\text{KO}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow 4\text{KOH}(s) + 3\text{O}_2(g)$$

If a reaction vessel contains 0.15 mol KO_2 and $0.10 \text{ mol H}_2\text{O}$, what is the limiting reactant? How many moles of oxygen can be produced?

28. How many grams of HCl react with 5.0 g of MnO₂ according to the equation.

$$4HCl(aq) + MnO_2(s) \rightarrow 2H_2O(l) + MnCl_2(aq) + Cl_2(g)$$
 [Ans. 8.40 g]

- **29.** 0.5 mol of H_2S and SO_2 are mixed together in a reaction flask in which the following reaction takes place: $2H_2S(g) + SO_2(g) \rightarrow 2H_2O(l) + 3S(s)$ Calculate the number of moles of sulphur formed. [Ans. 0.75 mol]
- **30.** Pure oxygen is prepared by thermal decomposition of KC1O₃ according to the equation :

$$KClO_3(s) \xrightarrow{\Delta} KCl(s) + \frac{3}{2}O_2(g)$$

Calculate the volume of oxygen gas liberated at STP by heating 12.25 g KClO₃(s). [Ans. 3.36 L]

- **31.** The density (in g mL⁻¹) of a 3.60 M sulphuric acid solution that is 29% H_2SO_4 (Molar mass = 98g mol⁻¹) by mass will be..... [Ans. 1.21 g/ml]
- 32. The cost of table salt (NaCl) is Rs. 10 per Kg. calculate its cost per mole.

 (Moar mass of NaCl is 58.5 gmol⁻¹)

 [Ans. 0.58 Rs.]
- 33. Mole fraction of the solute in a 1.00 molal aqueous solutioon is......

[Ans. 0.0177]

35. Calculate the percentage of N in urea. (Molar mass of urea = 60 g mol^{-1}] [Ans. 46.66%]

36. 7.5 grams of gas occupy 5.6 Litres of volume at STP. The gas is

- (a) NO
- (b) N_2O
- (c) CO
- (d) CO_2

[Ans. NO]

- **37.** 25 mL of 3.0 M HCl are mixed with 75 mL of 4.0 M HCl. If the volumes are additive, the molarity of the final mixture will be. [Ans. 3.75 M]
- **38.** Hydrogen peroxide and water contain 5.93% and 11.2% of hydrogen respectively. Show that the data illustrate law of multiple proportions.
- 39. How many atoms and molecules are present in 124 g of phosphorus (P_4) ?
 [Ans. Atoms = 4 N_A & Molecules = N_A]

3 - Marks Questions

- 1. Give three main points of difference between a compound and a mixture.
- 2. Define homogeneous and heterogeneous mixture with example.
- 3. Write seven fundamental quantities & their units
- **4.** Pressure is defined as force per unit area of the surface. The SI unit of pressure, Pascal is :

$$1Pa = 1 Nm^{-2}$$

If mass of air at sea level is 1034 g cm⁻², calculate the pressure in Pascal.

[Ans.
$$1.01332 \times 10^5 \text{ Pa}$$
]

5. The following data are obtained when dinitrogen and dioxygen react together to form different compounds:

	(i)	(ii)	(iii)	(iv)
Mass of dinitrogen	14	14	28	28
Mass of dioxygen	16	32	32	80

Which law of chemical combination is obeyed by the above experimental data? Give its statement.

- **6.** Calculate:
 - (i) Mass in gram of 5.8 mol N₂O
 - (ii) Number of moles in 8.0 g of O₂
 - (iii) Molar mass if 11.2 L at STP weigh 8.5 g.

- 7. In three moles of ethane (C_2H_6) , calculate the following :
 - (i) Number of moles of carbon atom,
 - (ii) Number of moles of hydrogen atoms,
 - (iii) Number of molecules of ethane.

[Ans. (i) 6 moles, (ii) 18 moles, (iii)
$$1.81 \times 10^{24}$$
]

- **8.** 16 g of an ideal gas SO_x occupies 5.6 L at STP. What is its molecular mass? What is the value of X? [Ans. 64u, x = 2]
- **9.** Calculate the number of moles :
 - (i) 5.0 L of 0.75 M Na₂CO₃
 - (ii) 7.85 g of Fe
 - (iii) 34.2 g of sucrose $(C_{12}H_{22}O_{11})$ [Ans. (i) 3.75, (ii) 0.14, (iii) 0.1]
- 10. Calculate the number of atoms in each of the following:
 - (i) 52 moles of Ar. (ii) 52*u* of He (iii) 52*g* of He.

[Ans. (i)
$$3.13 \times 10^{25}$$
 (ii) 13 (iii) 7.83×10^{24}]

- 11. Vitamin C is essential for the prevention of scurvy. Combustion of 0.2000g of vitamin C gives 0.2998g of CO₂ and 0.819g of H₂O. What is the empirical formula of vitamin C?
- **12.** A compound contains 4.07% hydrogen, 24.27% carbon and 71.65% chlorine. Its molar mass is 98.96 g. What are its empirical and molecular formulas? [Ans. CH₂C1, C₂H₄Cl₂]
- 13. A compound made up of two elements A and B has A = 70%, B = 30%. Their relative number of moles in the compound is 1.25 and 1.88, calculate:
 - (i) Atomic masses of the elements A and B
 - (ii) Molecular formula of the compound, if its molecular mass is found to be 160. [Ans. (i) 56 and 16, (ii) A_2B_3]

- **14.** Calculate the mass of sodium acetate (CH₃COONa) required for making 500 mL of 0.375 molar aqueous solution. (Molar mass of sodium acetate is 82.0245 g mol⁻¹). [Ans. 15.375 g]
- **15.** Calculate the concentration of nitric acid in moles per litre in a sample which has a density, 1.41 g mL⁻¹ and the mass per cent of nitric acid in it being 69%. [Ans. 15.44 M]
- **16.** What is the concentration of sugar $(C_{12}H_{22}O_{11})$ in mol L⁻¹ if its 20 g are dissolved in enough water to make a final volume up to 2L? [Ans. 0.029 M]
- 17. Calcium carbonate reacts with aqueous HCl according to the reaction:

$$CaCO_3(s) + 2 HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M HCl? [Ans.0.94 g]

- 18. The reaction 2C + $O_2 \rightarrow$ 2CO is carried out by taking 24.0 g of carbon and 96.0 g of O_2 . Find out.
 - (i) Which reactant is left in excess?
 - (ii) How much of it is left?
 - (iii) How many grams of the other reactant should be taken so that nothing is left at the end of the reaction? [Ans. (i) O_2 , (ii) 64 g, (iii) 72]
- **19.** A 10 g sample of a mixture of calcium chloride and sodium chloride is treated with Na₂CO₃ to precipitate calcium as calcium carbonate. This CaCO₃ is heated to convert all the calcium to CaO and the final mass of CaO is 1.62 g. Calculate % by mass of NaCl in original solution.

[Ans. 67.9%]

- **20.** 3.0 gm of H_2 react with 29.0 gm of O_2 yield H_2O .
 - (i) Which is the limiting reagent?
 - (ii) Calculate the maximum amount of H₂O that can be formed.
 - (iii) Calculate the amount of the reactant left unreacted.

[Ans.
$$H_2$$
, 26.8g H_2O & 5.2 g O_2]

21. Zinc and hydrochloric acid react accordingly to the reaction:

$$Zn(s)$$
 + $2HCl(aq)$ \longrightarrow $ZnCl_2(aq)$ + $H_2(g)$

If 0.30 mol Zn are added to hydrochloric acid containing 0.52 mol of HCl,

How many moles of H₂ are produced?

[HCl is limiting reagent; H₂ formed = 0.36 mol]

22. How many moles of Lead (II) chloride will be formed from a reaction between 6.5g of PbO and 3.2 g of HCl? [Atomic mass of Pb = 207 u]

[Ans: 0.029 mole]

23. What volume of oxygen at N.T.P is needed to cause the complete combustion of 200 ml of acetylene? Also calculate the volume of carbon dioxide formed. [Ans: 500 mL of O₂ & 400 mL of CO₂]

5 - Marks Questions

1. (i) A black dot used as a full stop at the end of a sentence has a mass of about one attogram. Assuming that the dot is made up of carbon, calculate the approximate number of carbon atoms present in the dot.

[Ans.
$$5.02 \times 10^4$$
]

- (ii) Which one of the following will have largest number of atoms?
 - (a) 1g Au (s) (b) 1g Na (s) (c) 1g Li (s) (d) 1g of Cl₂(g)

- 2. (i) What is the difference between empirical formula and molecular formula?
 - (ii) A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gas 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calcuate (i) Empirical formula, (ii) molar mass of the gas, and (iii) Molecular formula.

- 3. (i) What is the difference between Molarity and Molality.
 - (ii) The Molarity of a solution of sulphuric acid is 1.35 M. Calculate its molality. (The density of acid solution is 1.02 g cm⁻³).[Ans. 1.52 m]
- **4.** (i) Define: (a) Mole fraction (b) Mass percentage.
 - (ii) If the density of methanol is 0.793 kg L^{-1} , what is its volume needed for making 2.5 L of its 0.25 M solution? [Ans. 0.0025 L]



Structure of **Atom**

• Information about fundamnetal particles of atom

Name of Constant	UNIT	Electron	Proton	Neutron
Mass	amu	0.000546	1.00728	1.008665
	kg	9.109×10^{-31}	1.673×10^{-27}	1.675×10^{-27}
Charge	Coloumbs	-1.602×10^{-19}	$+ 1.602 \times 10^{-19}$	Zero
	esu	-4.8×10^{-10}	$+4.8 \times 10^{-10}$	Zero
	Relative	– 1	+ 1	Zero

- **Electromagnetic radiations:** Energy emitted from any source (in forms of waves) in which electric and magnetic fields oscillated perpendicular to each other and travelling with a velocity of light is known as EM radiation.
- Characteristics of waves :
 - (a) Wavelength: The distance of one crest and one trough in a wave. Denoted by ' λ '.
- a λ
- (b) Frequency: Number of waves passing through a given point in one second.

Denoted by
$$\upsilon$$
.
$$\begin{bmatrix} \upsilon = \frac{1}{t} \implies \sec^{-1} \text{ or Hz} \\ t = \text{Time period} \end{bmatrix}$$

- (c) Amplitude: The height of crest or depth of a trough denoted by 'a'.
- (d) Wave Number : Number of waves per unit length denoted by $\bar{\upsilon}$

$$\frac{1}{v} = \frac{1}{\lambda} = cm^{-1} \text{ (or m}^{-1}\text{)}$$

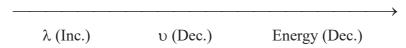
(e) Velocity: Linear distance travelled by a wave in one second.

velocity of light
$$c = \frac{\text{Distance}}{\text{Time}} = \lambda \times \frac{1}{t} = \upsilon \lambda$$

$$\vdots \qquad \qquad \upsilon \qquad = \frac{c}{\lambda}$$

• Energywise order for EM radiation.

 $cosmic < \gamma \, rays < X \, rays < UV < VIBGYOR < IR < Microwaves < Radiowaves$



- **Photon**: A packet or particle of light energy is knows as **Photon**.
- Planck's quantum theory: The energy emitted or absorbed by a source is discontinuous in form of small packet of energy, called quantum. Quantum of light is called **photon.**

• **Photo electric effect:** The phenomenon of ejection of electrons from a metal surface when a light of suitable frequency falls on metal surface.

$$h\upsilon - h\upsilon_0 = \frac{1}{2} \text{ mv}^2$$

 $hv \Rightarrow$ Energy of incident light on metal surface.

 $hv_0 \Rightarrow$ Work function of metal.

 $\frac{1}{2}$ mv² = Kinetic energy by which e^- is emitted from metal surface.

• **de Broglie equation :** All material particles in motion also exhibit wave like properties.

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

For microscopic particles mass is very less therefore Wavelength of wave associated with it can be detected.

For macroscopic particles mass is large, λ of wave associated with it can not be detected. Hence dominant wave character.

Hence microscopic bodies have dual nature, where as macroscopic bodies have particle nature.

Heisenberg's Uncertainty Principle

It is impossible to determine the exact position and velocity of a moving subatomic particle simultaneously with accuracy.

$$\Delta x \times m \Delta v \ge \frac{h}{4\pi}$$

 Δx = uncertainty in position

 $\Delta v = \text{uncertainty in velocity}$

Bohr's theory for H [H like one e^- systems He⁺; Li²⁺]

(1) e^- revolving round the nucleus in circular path [stationary state; SHELL] with a definite angular momentum $\frac{nh}{2\pi}[n \text{ no. of shell of } e^-]$ and with definite energy

$$E_{\rm n} = \left[\frac{-2\pi^2 m e^4 z^2}{n^2 h^2} \right] \Rightarrow -2.18 \times 10^{-18} \frac{Z^2}{n^2} \text{ J/Atom.}$$

(2) As n increases, Energy of e^- becomes less – ve [Due to less force of Proton attraction]

As n decreases, Energy of e^- becomes More – ve [Due to more force of attraction by protons]

(3) In infinity shell e^- has zero force of attraction therefore zero energy.

(4) Electron energy only changes by definite values $\Delta E = E_f - E_{i}$

Hydrogen spectrum : When e^- in hydrogen atom is provided energy it gets excited to higher shell from ground state, it comes back to ground state by emitting energy in definite values.

"Quanta": The emission of light energy is known as emission spectra. It corresponds to each atom depending upon which energy shell e^- is excited. It is **discontinuous** spectra as ' λ ' of light radiations do not merge with each other like in VIBGYOR (Continuous Spectra).

When e^- falls from any excited state to

$$\frac{1}{\lambda} = 1,09,678 \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] Z^2$$
 R = Rydberg constant = 109678 cm⁻¹

$$n_i = 1, n_f = 2, 3, 4, \dots$$
 [Lyman series] (UV)

$$n_i = 2, n_f = 3, 4, 5, \dots$$
 [Balmer series] (VIBGYOR)

$$n_i = 3, n_f = 4, 5, 6$$
 [Paschem series] IR.

$$n_i = 4, n_f = 5, 6, 7$$
 [Bracket series] IR.

$$n_i = 5, n_f = 6, 7, 8$$
 [Pfund series] IR.

Quantum numbers: The noumbers which **completely** define the **state** of e^- in an atom.

(1) Principal Quantum No.: It describes the distance of e^- from nucleus 'n' *i.e.*, defines the shell no. It is denoted by 'n'.

$$n = 1, 2, 3, 4, 5, \dots$$

K, L, M, N, O

(2) Azimuthal (*I*) Quantum No.: It defines the path of e^- decided by angular momentum of e^- . Each angular momentum value corresponds to one subshell. The no. of subshells in a shell is 0 to n-1.

n l(0 to n-1)

3

1 0
$$l=0$$
 's' subshell

2 0, 1
$$l=1$$
 'p' subshell

$$0, 1, 2$$
 $l=2$ 'd' subshell

4,
$$0, 1, 2, 3$$
 $l = 3$ 'f' subshell

All subshells are wave functions for locating e^- .

In the same shell energy increase s .

- (3) Magnetic Quantum No.: It gives the no. of magnetic orientations an e^- can have in a subshell. That is number of orbitals in a sub-shell. $m_s = -l......+ l = (2l + 1)$.
- (4) Spin Quantum No.: An e^- is continuously spinning on its own axis.

The value of
$$s = \frac{1}{2}$$
 or $-\frac{1}{2}$

An orbital can have maximum two e^- one with clockwise and other with anticlockwise spin.

Aufbau principle

- (a) Electrons are filled in increasing order of energy of sub-shell.
- (b) As 'n + l' value increases energy of e^- increases in that sub-shell.
- (c) For two sub-shells with same 'n + l' value, as 'n' value increases energy of e^- increases.

Pauli's principle

No two electrons can have same set of four quantum numbers in an atom.

Hund's rule of maximum multiplicity

The pairing of e^- in degenerate orbitals (different orbitals with same energy) will get paired only once they have been singly occupied with same spin.

Important Points

The filling of e^- in subshells follows this order. (As per Aufbau principle)

(A)
$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p$$

 $< 7s < 5f < 6d < 7p$

(B) Half filled and completely filled subshells have more **stability** than incompletely filled subshells.

$$Cr = [Ar] 4s^1 3d^5$$

 $Cu = [Ar] 4s^1 3d^{10}$

- (C) As the shell no. inc. size of subshell increases e.g., size of (2s > 1s); (3p > 2p); (4d > 3d)
- (D) The region in an orbital where probability of finding the e^- is zero is known as **Nodal plane** (or Node).

The no. of [radial nodes] = n - l - 1 & Angular Nodes = l, Total nodes = n - 1.

(E) ψ (psi)	ψ²(psi square)
A wave function for locating an electron	The square of wave function where the probability of finding the e^- is maximum.
	[Each value of ψ^2 is a region and defines one orbital]

(F) Orbit

- (1) A definite distance from the nucleus for finding the e^- [e^- as a particle]
- (2) It has definite size and e^- in this orbit has definite energy.

Orbital

- (1) A probability region for locating the e⁻ around the nuclues.
 It is a wave function [e⁻ as a wave]
- (2) It does not define definite size. But only a boundary region diagram of a wave for locating the e^- .

STRUCTURE OF ATOM

A. Fundamental particles of an atom, Electromagnetic Spectrum & Bohr's Theory

1 - Mark Questions

- Q. 1. If the length of the crest of a wave is 4 pm. Write the wavelength of this wave.

 [Ans.8 pm]
- Q. 2. A radiation emitted from a hot iron is photon or quantum?

- Q. 3. The line spectrum of an element is known as fingerprints of its atom.

 Comment
- **Q. 4.** What is the value of the Bohr's radius for the first orbit of hydrogen atom?
- **Q. 5.** Distinguish between a photon and a quantum.
- Q. 6. What type of metals are used in photoelectric cell? Give one example.

[Ans. With large size, less work function.]

- Q. 7. Which series of lines of the hydrogen spectrum lie in the visible region'?
- Q. 8. Cs shows maximum photoelectric effect, why?
- **Q. 9.** Mention the physical significance of ψ and ψ^2 .
- **Q. 10.** Why did Heisenberg's uncertainty principle replaces the concept of definite orbit by the concept of probability?
- Q. 11. What is uncertain in uncertainty principle?
- Q. 12. Can a moving cricket ball have a wave character? Justify your answer.
- Q. 13. Heisenberg uncertainty principle has no significance in our everyday life. Explain.
- **Q. 14.** Out of the *d* orbitals which does not have four lobes?
- Q. 15. Write the Schrodinger wave equation.
- **Q. 16.** Why uncertainty in position is more when uncertainty in velocity is less for an electron?
- **Q. 17.** What is the lowest value of n that allows g orbitals to exist?
- **Q. 18.** What are the four quantum numbers of 19th electron of copper?

(**Given :** Atomic number of copper = 29)

- **Q. 19.** Which quantum number is not obtained from solution of Schrödinger wave equation?
- Q. 20. How many electrons will be present in the sub-shells having m_s , value of -1/2 for n = 4?
- **Q. 21.** Write the electronic configuration of Ni^{2+} . (At. No. of Ni = 28)
- Q. 22. How many radial and angular nodes are present in 2p orbital.

[Ans. Radial nodes = 0, Angular nodes = 1]

- **Q. 23.** Which of the following orbitals are possible? 1p, 2s, 2p and 3f
- Q. 24. Write the name of non-directional subshell.
- Q. 25. Write the name of quantum number which determines the orientation of orbitals.
- Q. 26. Write the name of quantum number which determines the shape of orbitals.
- **Q. 27.** Using s, p, d notations, describe the orbital with the following quantum numbers :

(a)
$$n = 4$$
, $l = 2$ (b) $n = 1$, $l = 0$. [Ans. (a) $4d$ (b) $1s$]

- Q. 28. How many orbitals are present in 'g' subshell?
- Q. 29. How many total electrons can be filled in all orbitals with (n+l) = 5? [Ans. 18 electrons $(4p^6 3d^{10} 5s^2]$]
- Q. 30. Name the dipositive ion represented by the electronic configuration $: 1s^2 2s^2 2p^6 3s^2 3p^6$. [Ans. Ca²⁺]
- **Q. 31.** Is it correct to say that every atom with even atomic number has all electron paired?
- Q. 32. Cr in ground state has how many unpaired electrons. (Cr, Atomic number = 24).
- **Q. 33.** Which has more energy of electron 4p or 5s?
- Q. 34. Nitrogen has correct configuration of $1s^2$, $2s^2$, $2p_x^{-1}$, $2p_y^{-1}$, $2p_z^{-1}$ is described by which principle?
- Q. 35. What are degenerate orbitals?

- **Q. 1.** Define black body and black body radiations.
- Q. 2. Give the essential postulates of Bohr's model of an atom. How did it explain?
 - (i) the stability of the atom?
 - (ii) origin of the spectral lines in H-atom?

- Q. 3. What is quantisation? How quantisation of energy was introduced in Bohr's model?
- **Q. 4.** What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition n = 4 to n = 2 of He⁺spectrum?

[Ans.
$$n_1 = 1$$
 and $n_2 = 2$]

Q. 5. What transition of Li²⁺ spectrum will have the same wavelength as that of the second line of Balmer series in He⁺spectrum?

[**Ans.**
$$n_2 = 6$$
 to $n_1 = 3$]

Q. 6. Calculate the energy required for the process

$$He^{+}(g) \longrightarrow He^{2+}(g) + e^{-}$$

The ionization energy for the H atom in the ground state is $2.18 \times 10^{-18} \, \text{J atom}^{-1}$ [Ans. $8.72 \times 10^{-18} \, \text{J}$]

- Q. 7. Calculate the wave number for the longest wavelength transition in the Balmer series of atomic hydrogen. [Ans. $1.523 \times 10^6 \text{ m}^{-1}$]
- Q. 8. To which orbit the electron in H atom will jump on absorbing 12.1 eV energy? [Ans. 3rd orbit]
- Q. 9. Calculate the energy associated with the first orbit of He⁺. What is the radius of this orbit? [Ans. 54.38 eV, 0.2645 Å]
- Q. 10. What is the distance of separation between 3rd and 4th orbit of H-atom? [Ans. 3.703 Å]
- Q. 11. The energy of electron in the first Bohr's orbit is -13.6 eV. Calculate the energy of electron in the first excited state. [Ans. -3.4 eV]
- Q. 12. Calculate the number of protons emitted in 10 hours by a 60 W sodium lamp emitting radiations of wavelength 6000 Å.
- Q. 13. Which one has a higher energy, a photon of violet light with wavelength 4000 Å or a proton of red light with wavelength 7000 Å?

[Given.
$$h = 6.62 \times 10^{-34} J sec.$$
]

Q. 14. A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of protons emitted per second by the bulb.

[Ans.
$$2.012 \times 10^{20} \, s^{-1}$$
]

- Q. 15. What are the maximum number of emission lines when the excited electron of a H atom in n = 4 drops to the ground state? [Ans. 6]
- **Q. 16.** Which has more energy, light radiation of wavelength 400 pm or light radiation of frequency 10¹⁵ Hz?
- **Q. 17.** Find the energy of electron in 4th shell of Li^{2+} ion.
- **Q. 18.** What is the wave number of an electron with shortest wavelength radiation in Lyman spectrum of He⁺ ion?
- **Q. 19.** Write short note on:
 - (a) Continuous and discontinuous spectrum.
 - (b) Absorbtion and emission spectrum.
- Q. 20. Calculate the mass of the photon with wavelength of 3 .6 Å.

[Ans.
$$6.135 \times 10^{-29} \text{ kg}$$
]

- Q. 21. Calculate the mass of the photon with wavelength of 5 pm.
- Q. 22. On the basis of uncertainty principle show that an electron cannot exist with in atomic nucleus. (Given: Nuclear radius = 10^{-15} m)

[Hint: Taking 10^{-15} m as Δx , the Δv comes much higher than the velocity of light and hence is not possible]

- Q. 23. Explain why the uncertainty principle is significant only from the motion of subatomic particles and is negligible for macroscopic particles?
- **Q. 24.** List two differences between orbit and orbital.
- Q. 25. Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around the orbit
- Q. 26. Comment on "Bohr's model is against the Heisenberg uncertainty principle".
- **Q. 27.** What are the similarities and difference in 2s and $2p_x$ orbitals and 1s and 2s orbitals?
- **Q. 28.** Draw shape of $d_{x^2-y^2}$ orbital.

- Q. 29. On the basis of Pauli's exclusion principle show that the maximum number of electrons in the M -shell (n = 3) of any individual atom is 18.
- **Q. 30.** Designate each subshell with n = 4.
- Q. 31. List the possible values for all the quantum numbers for the following subshell.

(a) 2p

(b) 4*f*

- Q. 32. Write down the electronic configuration of Fe^{3+} and Ni^{2+} . How many unpaired electrons are present? (Given Atomic number, Fe=26, Ni=28).
- Q. 33. Out of principal, angular, magnetic and spin quantum number, which quantum number determines the ?
 - (a) Shape of the orbital
 - (b) Number of orbitals in an orbit
 - (c) Size of the orbital
 - (d) Spin orientation of the electron.
- **Q. 34.** What is the Hund's rule of maximum multiplicity? Explain with suitable example.
- **Q. 35.** Explain why:
 - (a) The three electrons present in 2p subshell of nitrogen remain unpaired.
 - (b) Cr has configuration $3d^5 4s^1$ and not $3d^4 4s^2$.
- Q. 36. (a) What is difference between 'l' and 'L'?
 - (b) Nitrogen has 7 proton, 7 electron and 7 neutrons. Calculate the number of electron, protons and neutrons in N³⁻ ion.
- **Q. 37.** Which one is having higher energy?
 - (a) Last electron of Cl⁻ or last electron of O²⁻.
 - (b) n = 4, l = 3 or n = 5, l = 2.

- **Q. 1.**(i) The energy associated with the first orbit in the hydrogen atom is $-2.18 \times 10^{-18} \,\text{J}$ atom⁻¹. What is the energy associated with the fourth orbit?
 - (ii) Calculate the radius of Bohr's third orbit for hydrogen atom.

[**Ans.**–
$$1.36 \times 10^{-19} \text{ J atom}^{-1}.4.761 \text{ nm}$$
]

- Q. 2. A bulb emits light of wave length 4500Å. The bulb is rated as 150 watt and 8% of the energy is emitted as light. How many photons are emitted by the bulb per second? [Ans. $n = 27.2 \times 10^{18}$]
- Q. 3. When light with a wavelength of 400 nm falls on the surface of sodium, electrons with a kinetic energy of 1.05×10^5 J mol⁻¹ are emitted.
 - (a) What is the minimum energy needed to remove an electron from sodium?
 - (b) What is the maximum wavelength of light that will cause a photoelectron to be emitted?

[Ans.
$$a = 3.2255 \times 10^{19} \text{ J}, b = 616 \text{ nm}$$
]

- Q. 4. Compare the frequency of light radiations emitted when electron falls from 5th shell to the 2nd shell in Li²⁺ ion and electron falls from 4th shell to the 1st shell in He⁺ ion.
- Q. 5. Calculate the number of waves made by Bohr electron in one complete revolution in its third orbit. [Ans. 3]
- Q. 6. What should be the ratio of velocities of CH_4 and O_2 molecules so that they are associated with de Broglie waves of equal wavelength? [Ans. 2]
- Q. 7. Calculate the wavelength of an electron that has been accelerated in a particle accelerator through a potential difference of 1 kv.

[Given
$$1eV = 1.6 \times 10^{-19} J$$
] [Ans. $3.87 \times 10^{-7} m$]

- Q. 8. (i) Discuss the similarities and differences between a 1s and 2s orbital. (ii) Draw the shape of d_{z^2} .
- Q. 9. Calculate the wavelength of a tennis ball of mass 60 gm moving with a velocity of 10 m per second. $(h = 6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1})$

[Ans. 10^{-3} metre]

Q. 10. Calculate the wavelength of 1000 kg rocket moving with a velocity of 3000 km/hr. $(h = 6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1})$

[Ans.
$$7.9512 \times 10^{-40}$$
 m]

Q. 11. Calculate the uncertain it in the velocity of a cricket ball of mass 150 g, if uncertainty in its position is of the order of 1 Å.

[Ans.
$$3.5 \times 10^{-24} \text{ m s}^1$$
]

- Q. 12. (a) What is de-Broglie wavelength for an electron moving with velocity of light?
 - (b) What is the angular momentum of electron in 5th shell?
- Q. 13. Two particles A and B have wavelength $\lambda_A = 5 \times 10^{-10}$ m and $\lambda_B = 10 \times 10^{10}$ m. Find their frequency, wave number and energies. Which has more penetrating power and why?
- **Q. 14.** (a) Which has max. uncertainty regarding position and why? Electron, proton and neutron.
 - (b) Find the number of waves associated with a light radiation of time period 5 ns.
- Q. 15. If an electron in He⁺ has angular momentum of $5h/2\pi$. Find its energy and wavelength associated with it. Find the kinetic energy of this electron.
- **Q. 16.** (i) An atomic orbital has n = 2. What are the possible values of l and m_l ?
 - (ii) List the quantum numbers $(m_1 \text{ and } l)$ of electrons for 3d orbital.
 - (iii) Which of the following orbitals are possible? 2*d*, 1*s*, 2*p* and 3*f*.
- **Q. 17.** (a) Write the maximum number of electron in a subshell with l = 3 and n = 4.
 - (b) Write the maximum number of electron that can be associated with the following set of quantum numbers?

$$n = 3$$
, $l = 1$ and $m_l = -1$

- (c) Write the maximum number of electron that can be accommodated in an atom in which the highest principal quantum number value is 4.
- Q. 18. (i) Write the electronic configurations of the following ions:

(a)
$$H^{-}(b)Na^{+}(c)O^{2-}(d) F^{-}$$

- (ii) What are the atomic numbers of elements whose outermost electrons are represented by (a) $3s^1(b) 2p^3$ and (c) $3p^5$?
- (iii) Which atoms are indicated by the following configurations?
 - (a) [He] $2s^1$ (b) [Ne] $3s^2 3p^3$ (c) [Ar] $4s^2 3d^1$.
- Q. 19. Calculate:
 - (a) Total number of spherical nodes in 3p orbital.
 - (b) Total number of nodal planes in 3p orbital.
 - (c) Nodal planes in 3*d* orbital.

- **Q. 1.**(a) Define Photoelectric effect? Mention its one practical application in daily life.
 - (b) Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate threshold frequency (v₀) and work function (W₀) of the metal.

[Ans.
$$v_o = 4.41 \times 10^{14} \text{ s}^{-1} \text{ W}_o = 2.92 \times 10^{-19} \text{ J}]$$

- Q. 2.(a) The electronic energy in Bohr's orbit is negative .How will you account for it?
 - (b) The ionisation energy of hydrogen atom is 13.6 eV. What will be the energy of the first orbit of He⁺ and Li²⁺ ions?

[Ans.
$$E_1$$
 of $He^+ = -54.4$ eV, E_1 of $Li^{2+} = -122.4$ eV]

- Q. 3.(a) Define the following terms:
 - (i) Threshold frequency
- (ii) Work function.
- (b) The work function for Cs atom is 1 .9 eV. Find threshold wavelength (λ_0) and threshold frequency (ν_0) of this light radiation. If Cs metal is irradiated with a radiation of wavelength 500 nm find kinetic energy and velocity of emitted electron.
- Q. 4.(a) State de Broglie equation. Write its significance.
 - (b) A beam of helium atoms moves with a velocity of 2.0×10^3 m s⁻¹. Find the wavelength of the particle constituting the beam

$$(h = 6.626 \times 10^{-34} \,\mathrm{J s}) \,[\mathrm{Ans.} \,49.9 \,\mathrm{pm}\,]$$

Q. 5.(a) State Heisenbergs uncertainty principle. Give its mathematical expression. Also give its significance.

(b) Calculate the uncertainty in the position of a dust particle with mass equal to 1 mg if the uncertainty in its velocity is $5.5 \times 10^{-20} \text{ms}^{-1}$.

[Ans.
$$9.55 \times 10^{10}$$
 m]

- Q. 6.(a) Cricket ball, a tennis ball and a proton which has more uncertainty in velocity and which follows Heisenberg uncertainty principle maximum.
 - (b) What is the similarity in de-Broglie and Heisenberg principle? Which is different from Bohr theory for structure of atom?
 - (c) Why energy in a given subshell is negative?
- Q. 7.(a) Write short notes on:
 - (i) Aufbau principle (ii) Pauli's principle (iii) Hund's rule.
 - (b) Write the electronic configuration of the following ions:
 - (i) Fe³⁺ (ii) Cu⁺ [Given Atomic number of Fe and Cu are 26 & 29]
- Q. 8.(a) Draw the shapes of the following orbitals.
 - (i) $3d_{xy}$ (ii) d_{z^2}
 - (b) What is the total number of orbitals associated with the principal quantum number n = 3?
 - (c) Using s, p, d, f notations, describe the orbital with the following quantum numbers:-

(a)
$$n = 3$$
, $l = 0$, (b) $n = 4$, $l = 2$, (c) $n = 5$, $l = 3$, (d) $n = 1$, $l = 0$

- **Q.9.** Explain the following:
 - (i) Energy of electron is not decided by : n, l, m and s.
 - (ii) Maximum number of electron with -1/2 spin for n = 3 is 6,9,12 or none.
 - (iii) Maximum number of electron can be present for n + l = 4.
 - (iv) 3f subshell is not possible.
 - (v) Maximum number of electrons in a subshell is : (2l+1) or (4l+1) or n^2

- **Q. 10.**(a) A neutral atom has 2K, 8L and 15 M electrons. Find the total numbers of electrons in s, p, d and f subshell.
 - (b) How many unpaired electrons are present in the following ions : $Al^+,\,Cr^{2+},\,Co^{3+}\,and\,Mn^{2+}$

(Given Atomic number : Al=13, Cr = 24, Co = 27 & Mn = 25)

- (c) One electron is present in 4f subshell. What is the sum of $n + l + m_1 + m_s$ values assuming 'f' subshell follows 3 to + 3 order of filling electron.
- **Q. 11.** Answer the following:
 - (a) n + l value for 14^{th} electron in an atom.
 - (b) Increasing order of filling electron in 4f, 5p and 6d subshells.
 - (c) 'm' and 'l' value for last electron of Mg atom.

(Given atomic number of Mg is 12)

(d) Subshell in which last electron is present in Ga.

(Given Atomic number of Ga is 31)

(e) Sum of spin of all the electron in element having atomic number 14.





Chapter - 3

Classification Of Elements And Periodicity In

Properties

The first systematic classification of elements was provided by Russian chemist D.I. Mendeleev.

1. Mendeleev's periodic law

"The physical and chemical properties of elements are periodic functions of their atomic weight."

2. It was modified to Modern Periodic law:

"The physical and chemical properties of elements are periodic functions of their atomic numbers."

It is the long form of periodic table:

7 Horizontal rows are called Periods and 18 Vertical columns are called Group

Group-1 are called **Alkali metals** Group-2 are called **Alkaline earth metals**.

Group-15 are called **Pnicogens**Group-16 are called **Chalcogens**Group-17 are called **Halogens**Group-18 are called **Noble gases**

3. 1st period—2 elements 2nd and 3rd period—8 elements

4th and 5th period—18 elements 6th period—32 elements

7th period—Incomplete (32 elements)

4. Groups

1 and 2 — 's' block elements last electron entered in 's' subshell $[s^1, s^2]$

3 to 12 — 'd' block elements last electrons entered in 'd' subshell $[d^1 \text{ to } d^{10}]$.

13 to 18 — 'p' block elements last electrons enter in 'p' subshell $[p^1 \text{ to } p^6]$.

Two *f*-block series lanthanoids and actinoids are placed in the bottom of periodic table.

5. (A) In 's' and 'p' block elements the electrons enters in outer most shell. In 'd' block elements the electron enters in the penultimate shell (n-1).

'f' block elements last electron enter the antepenultimate shell (n-2).

(B) 'f' block elements are placed in between 'd' block elements.

'f' block elements in 2 rows [4f lanthanoids, 5f actinoids]

6. General outer electronic configuration

's' block: ns^1 , ns^2 [Group 1 to 2]

'p' block: ns^1np^1 to ns^2np^6 Group 13 to 18

'd' block: $ns^{0-2}(n-1) d^{1 \text{ to } 10}$ Group 3 to 12

'f' block: $(n-2)f^{1 \text{ to } 14}(n-1)d^{0,1}ns^2$

7. General periodic trends in properties of elements

Atomic Radius

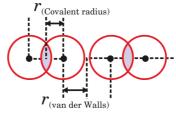
- (A) Left to right decreases due to effect of successive increasing nuclear change without addition of a new shell.
- (B) From top to bottom atomic radius increases due to successive addition of shell.
- (C) Noble gases have large radius than **group 17** due to complete filling of electron in outer shell electron-electron repulsion mildy increases.

Covalent radius

It is half of the distance between the centre of nuclei of two adjacent similiar atoms which are bonded to each other by single covalent bond.

van der waal's radius

van der waal's radius is defined as one-half the distance between the centres of nuclei of two nearest like atoms belonging to two adjacent molecules of the element in the solid state.



Metallic radius

Half of the distance between the centres of the nuclei of two adjacent atoms in the metallic crystal. A comparision of the three atomic radii show that van der waal's radius is maximum while the covalent radius has the least value.

van der waal's radius > Metallic radius > Covalent radius

Ionic radius (A) Cation radius < Atomic radius—due to more no. of protons than

number of electron coloumbic force increases, size decreases.

$$[Mg^{2^+} < Mg^+ < Mg]$$

(B) Anion radius > Atomic radius—Due to more number of electron than number of protons

$$[N^{3-} > O^{2-} > F^{-}]$$

Electron-Electron repulsion increase, coloumbic force of attraction decreases.

(C) For Isoelectronic species—More is the charge of cation lesser the size. More is the charge of anion, more is the size.

(D) Size —
$$O^{2-} > F^- > Na > Na^+ > Mg^{2+}$$

8. (A) Ionization energy:

The minimum amount of energy which is required to remove the most loosely bound electron from an isolated atom in the gaseous state is called Ionization enthalpy.

Variation of I.E along a period:

Ionization energy increase along the period because atomic radii decrease and nuclear charge increase along the period.

Variation down the group:

Inozation energy decrease down the group because atomic radius increase down the group.

Metallic behaviour : Decrease from left to right due to increase in ionization enthalpy.

Non metallic behaviour: Increase from left to right due to more number of electron in outershell and added electron goes towards nucleus.

(9) Screening effect or shielding effect:-

It is the decrease in the force of attraction between nucleus and outermost electron due to presence of inner shell electrons. As a result, the outer most

electrons does not feel full charge of the nucleus. The actual charge felt by an electron is called effective Nuclear charge.

Shielding effect is in the following order

d & f subshell show weak sheilding effect because their orbital size are large and are more diffused.

(10) Isoelectronic species:

Ions of different elements which have the same number of electons but different no. of protons are called isoelectronic ions.

	Na^+	Mg^{2+}	$A1^{3+}$	N^{3-}	O^{2-}	F^{-}
No. of Protons	11	12	13	7	8	9
No. of electrons	10	10	10	10	10	10
Ionic Radii	$Al^{3+} <$	$Mg^{2+} <$	Na ⁺ <	F- <	O^{2-} <	N^{3-}

(11) Electron gain enthalpy:

The enthalpy change when an extra electron is added to neutral gaseous atom to form anion.

$$E(g) + e^{-} \longrightarrow E^{-}(g)$$

- **Trends**—**From left to right**—Increase due to decrease in size, more attraction of added electron by nucleus.
- From top to bottom—Decreases as the added electron is away from nucleus due to increase in size.
- Cl has more negative electron gain enthalpy than fluorine—Due to small size of fluorine extra added electron has more inter electronic repulsion than chlorine which has large size.
- Similarly Phosphorus and Sulphur have negative electron gain enthalpy than nitrogen and oxygen respectively.
- Maximum electron gain enthalpy—Chlorine (in periodic table)
- Electron gain enthalpy—
 Halogen > Oxygen > Nitrogen > Metal of group 1 and 13 and non metal of group 14 > metal of group 2.
- 2nd electron gain enthalpy is always positive.

(12) Electro negativity:

The tendency of an atom to attract the shared pair of electron towards itself in a bonded state.

- # Fluorine is the most electronegative element in the periodic table.
- # Cesium is the least electronegative element in the periodic table.
- # Electronegativity is decrease down the group and increase along the period.

Difference between electron gain enthalpy and Electronegativity.

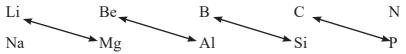
Electron gain enthalpy is the energy, but electronegativity is not the energy, it is only the tendency of an atom in a molecule to attract the shared pair of electrons. Three highest electronegative atoms F > O > N.

Maximum electronegative Assign to F.

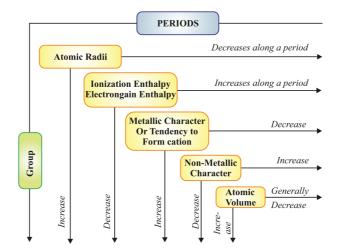
- * Lightest element : **Hydrogen**
- * Lightest metal : Lithium
- * Heaviest metal (highest density) : **Osmium**
- * Most reactive metal : Caesium
- * Most reactive nonmetal : Fluorine
- * Most malleable metal : **Gold**
- * Electrically best conductor : **Silver**
- * Metals which are relatively volatile: **Zn**, **Cd**, **Hg**
- * Strongest reducing agent in aqueous solution : Lithium
- * Strongest oxidising agent : Fluorine
- * The element of lowest ionization energy: Caesium
- * The element of highest ionization energy : **Helium**
- * The most electronegative element : Fluorine
- * The element of highest electron gain enthalpy: Chlorine
- * The group containing most electropositive metals : Group 1
- * The group containing most electronegative metals : Halogens Group 17
- * The group containing maximum number of gaseous elements : Group 18

(13) Second period element—Show different behaviour that I group element—Due to (a) small size (b) High electron negativity (C) High polarising power (d) absence of 'd' orbital.

(14) The similarities in properties of first member of a group to second member of just next higher group due to comparable atomic radius, nearly same polarising power of ions is known as **diagonal relationship**.



Elements with number of e-		in valance shell		
(a)	1, 2, 3	metals		
(b)	4	metalloids		
(c)	5, 6, 7	non-metals		
(d)	8	noble gas		



1 -Mark Questions

- 1. Metals are placed on which side of modern periodic table?
- 2. Which pair of elements has similar properties ? $\begin{bmatrix} 13, & 31 \\ 11, & 21 \end{bmatrix}$ [Ans. 13, 31]
- 3. Which atomic number refers to a non-metal elements? [Ans. 17, 35]

- 4. Eka Aluminium & Eka silicon are known as and
- **5.** (a) Name the element which exhibit diagonal relationship with Be.
 - (b) Which group elements are known as chalcogens?
- **6.** Which pair of elements are 's' block elements ? $\begin{bmatrix} 37, & 38 \\ 55, & 37 \end{bmatrix}$ [Ans. Both]
- 7. The element with ns^2 , np^5 configuration is non-metal or metal?
- 8. Define van der waal's radius.
- **9.** Write the outer shell configuration of atomic number 31. [Ans. $4s^2 4p^1$]
- **10.** Find the group number and period number of element having atomic number 52. [Ans. Period = 5th, Group = 16th]
- 11. Arrange O^{2-} , O^{-1} , O in decreasing radius (size). [Ans. $O^{2-} > O^{-1} > O$]
- **12.** Which element is iso-electronic with Na⁺? (Given Na atomic number: 11) [Ans. Ne]
- **13.** Why noble gas have bigger size than halogens?
- **14.** An element is placed in 5th period and 3rd group what is its atomic no. ? [Ans. 39]
- 15. Why first electron gain enthalpy of sulphur is more negative than oxygen?
- **16.** Write general outer electronic configuration of 4f series elements.

[Ans.
$$6s^2$$
 $5d^{0-1}$ $4f^{1 \text{ to } 14}$]

- 17. Write the IUPAC name of element with atomic number 115, 107.
- **18.** Write two isoelectronic species with Br (35). [Ans. $Kr^+ Se^{-1}$]
- 19. What is covalency of Al in $[AlCl_4]^-$? [Ans. 4]
- **20.** Write the IUPAC Symbol for the element having atomic number 120. [Ans. Ubn]
- 21. Show that 4th period can have maximum 18 elements in it.
- 22. Second IE is always more than first IE, why?
- **23.** Electronegativity of F > Cl > Br > I, why?
- **24.** Arrange F and Cl in terms of increasing chemical reacitity.
- **25.** Second IE of Na is more than second IE of Mg. Why?
- **26.** $\Delta_{\rm eg} H^{\Theta}_{1}$ is exothermic while $\Delta_{\rm eg} H^{\Theta}_{2}$ is endothermic, justify.

- **27.** IE for cation is more than neutral atom. Why?
- 28. Define diagonal relationship with the help of an example.
- **29.** Out of O⁻ and O, which has more negative electron gain enthalpy?

- 1. Cations are smaller than their parent atom whereas anions are larger in size than their parent atom. Explain.
- 2. Ionization energy of nitrogen is more than 'O' and 'C' both, why?
- **3.** First ionization energy of boron is less than Be but size of Be is less than Boron. Why?
- 4. Electron gain enthalpy of Mg is positive. Explain.
- **5.** Define Covalency
- **6.** The reactivity of halogens decrease down the group but of alkali metals increases down the group. Why?
- 7. Name a halogen, a metal and a group13 element which are liquid at 30°C. [Ans. Br, Hg, Ga]
- **8.** The reducing power of elements increases down the group but reverse is true for oxidising power along a period. Why?
- **9.** What is the formula of binary compound formed between:
 - (a) 1st element of 1st group and iodine.
 - (b) 2nd element of 2nd group and 1st element of 17th group.
- **10.** Arrange in the following in increasing order of property indicated:
 - (a) Size I, F, Cl, Br
 - (b) Oxidising power I, F, Br, Cl
- 11. Oxygen is more non-metallic than nitrogen but less than fluorine why?
- 12. LiCl, LiBr, LiI are covalent as well as ionic why?
- **13.** PbCl₂ is more stable than PbCl₄. Why? [Ans. Inert pair effect]
- **14.** [Magnesium and Lithium both form nitrides why?
- **15.** Which has least IE $[3p^3, 3p^6, 2p^3, 2p^6]$?
- **16.** (a) IE of sulphur is lower than chlorine.
 - (b) Arrange the following in decreasing order of their electronegativity: F, O, N, Cl, C, H.

- 17. Element 'A' in group 17 (2nd period)
 - 'B' in group 16 (2nd period)
 - 'C' in group 15 (2nd period)

Arrange 'A', 'B' and 'C' in their decreasing order of electronegativity and ionization enthalpy.

- **18.** Element 'A' 13 group forms ionic compounds. Write the :
 - (a) Formula of its oxide.
 - (b) Arrange the following in their decreasing electropositive character Mg, Na, Al, Si.
- 19. Write the atomic number of element place diagonally to:
 - (a) Group 14, period 4
- (b) Group 2, period 5
- (c) Group 17, period 4
- **20.** An element has outer shell electronic configuration $4s^2 4p^3$. Find :-
 - (a) The atomic number of element place next below it.
 - (b) Atomic number of next noble gas.

3 - Mark Ouestions

- 1. What is metallic radius, Covalent radius, van der waal's radius. Give one example for each.
- 2. Oxygen has first electron gain enthalpy exothermic while second endothermic still a large number of ionic oxides are formed. Why?
- **3.** In some properties Boron shows different properties with respect to rest of the membering the group. Justify.
- 4. Out of group 17, 18 and I, predict:-
 - (a) Which has most negative first electron gain enthalpy?
 - (b) Which shows most metallic behaviour?
 - (c) Which has highly positive electon gain entalpy?
- 5. What are (a) representative elements, (b) Transition elements, (c) Lanthanoid and actinoids. Give their positions in modern periodic table.
- 6. Why LiF, NaF, KF, RbF, CsF are ionic? But LiF is less ionic than CsF.
- 7. (a) Why Ca has larger atomic radius than Al?
 - (b) Why $2s^2 e^-$ is difficult to remove than 2p electron?
- 8. (a) Why the compounds of group 17 with group 13 elements are more

ionic and stable than with (group 1) elements? (b) Na₂O is more ionic than Li₂O. why?

9. Explain the following data :

Ionization energy Cl < H < O < N < F.

- 10. IE₂ of 3^{rd} period elements is as follows. Why? Mg < Si < Al < P < S < Cl < Ar < Na.
- 11. Account fot the following:
 - (a) Halogens have very high negative electron gain enthalpy
 - (b) The electron gain enthalpy of Cl (Z = 17) is more negative than that of Fluorine (Z = 9).
 - (c) Ionization enthaply of Nitrogen (Z = 7) is more than oxygen (Z = 8).
- **12.** What are the d- block elements? Write any four properties of d block elements and give their general outer electronic configuration.
- **13.** Explain the following:
 - (a) Modern Periodic law. (b) Electronegativity (c) Shielding effect
- **14.** Among the second period elements the actual ionization enthalpies are in the order Li \leq B \leq Be \leq C \leq O \leq N \leq F \leq Ne. Explain why?
 - (i) Be has higher $(\Delta iH)_1$ than B (ii) O has lower $(\Delta iH)_1$ than N and F?
- **15.** What do you understand by the isoelectronic species ? Name a species that will be isoelectronic with each of the following atoms or ions.
 - (i) F- (ii) Ar (iii) Ca2+ (iv) Rb+
- **16.** (a) Show by a chemical reaction with water that Na₂O is a basic oxide and Cl₂O₇ is an acidic oxide.
 - (b) Name a species that will be isoelectronic with each of the following atoms or ions, (i) F^- (ii) Ca^{2+}
- 17. The first ionization enthalpy values (in kJmol⁻¹) of group-13 elements are:

How would you explain this deviation from the general trend?

18. The first (IE₁) and the second (IE₂) ionization enthalpies (kJ mol⁻¹) of three elements are given below:

	I	II	III
IE_1	403	549	1142
IE_2	2640	1060	2080

Identify the element which is likely to be:-

- (a) a non metal
- (b) an alkali metal
- (c) an alkaline earth metal

5 - Mark Questions

- 1. (A) Which of the following have same chemical properties:
 - (a) Atomic no. 17, 53
- (b) Atomic no. 8, 52

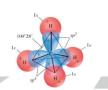
(c) Both

- (d) None
- (B) Answer the following:
 - (i) B, Al, Ga (decreasing order of atomic radii).
 - (ii) C, S, N (decreasing order of $(\Delta \text{Heg})_1$)
 - (iii) Al forms amphoteric oxide. Why?
 - (iv) Si is a semiconductor while 'C' is a non-metal, why?

2.	Element	$\Delta_i \mathbf{H}^\Theta_{ 1}$	$\Delta_{m{i}}\mathbf{H^{\Theta}}_{m{2}}$	$\Delta eg \mathrm{H}^{\Theta}{}_{1}$	
	I	1681	3374	-328	
	II	1008	1846	-295	
	III	2372	5251	+ 48	

- (a) The most reactive non-metal.
- (b) The least reactive non-metal.
- (c) The least reactive element. Give reasons also.

[**Ans.** (a) 1 (b) II (c) III]



Chapter - 4

Chemical Bonding And Molecular **Structure**

- 1. The interaction between two atoms which holds them together within a molecule or ions in known as chemical bond.
- 2. The elements with one, two, three, four, five, six or seven electrons is outer shell, use these electrons to complete octet. The electrons which take part in two or more atoms to complete octet is known as electrovalency.
- 3. Lewis symbols or electron dot symbols involve the presentation of valence electrons (outer electrons) in an atom $\dot{N}a$, $\dot{M}g$:, $\dot{A}\dot{l}$, $\dot{S}\dot{i}$. etc.
- **4.** Electrovalent bond or ionic Bond: The bond (chemical interaction) between two atoms formed by complete transference of electron from valence shell (outer shell) of an atom to another to complete octet is known as ionic bond.
- 5. This ionic bond is favoured by low ionization enthalpy of metal, high electron gain enthalpy of non-metal atom and high lattice enthalpy.
- 6. Characteristics of ionic compound: They are solids, a definite arrangement/ pattern of ion (to give crystalline solids), high melting point and boiling point, conductors in fused state and in aqueous medium, soluble in H₂O [Hydration].
- **7.** Lattice enthalpy: The energy released when one mole of ionic solid is formed from its ions in their gaseous state. Lattice energy is directly proportional to charge of ion and inversely proportions to size of ions *i.e.*, more is charge density, more is lattice enthalpy.
- 8. Mg \longrightarrow Mg²⁺ + 2e⁻ O + 2e⁻ \longrightarrow O²⁻
 (2, 8, 2) (2, 6)
 Mg²⁺ + O²⁻ \longrightarrow MgO Ionic compound [A crystalline lattice].

9. (a) Born Haber Cycle: For formation of ionic compound e.g., Na^+Cl^- .

$$Na_{(s)} \xrightarrow{S^{*}} Na_{(g)} \xrightarrow{IE} Na^{+}_{(g)}$$

$$\frac{1}{2}Cl_{2}(g) \xrightarrow{\frac{1}{2}D} Cl_{(g)} + e^{-} \xrightarrow{(\Delta Heg)_{1}} Cl^{-}_{(g)}$$

$$\Delta H_{j} \text{ of NaC} l = S + IE + \frac{1}{2}D + \Delta Heg + LE$$

$$S = \text{Sublimation Enthalpy}$$

$$IE = \text{Ionization Enthalpy}$$

$$D = \text{Bond Dissociation Enthalpy}$$

$$(\Delta Heg)_{1} - \text{First electron gain Enthalpy}$$

$$LE = \text{Lattice Energy}$$

- (b) Ionic bonds are Non directional in nature.
- **10. Fajan's Rule :** Polarizability and polarizing power. The power of a cation to distort the negative field of an anion is called polarising power and the tendency of anion to get distorted its negative field by a cation is known as polarizability. Factors affecting polarizing power and polarizability are:
 - (a) High charge and small size of cation.
 - (b) High charge and large size of anion.
- 11. Covalent Bond: Lewis Langmuir Concept

The (chemical interaction) bond formed by mutual sharing of electrons between combining atom as to complete their octets is known as covalent bond and no. of electrons involved is called their covalency.

- **12. Formal charge :** [Total no. of valence e^- in free atom] [Total no. of non bonding electrons] $\frac{1}{2}$ [Total no. of shared electrons]
- **13.** The valence bond approach: (a) The two atomic orbitals with one electron each, overlap to give maximum electron density region common to both atoms is known as single covalent bond

- (b) The strength of covalent bond is proportional to extent of overlapping between the atomic orbitals of valence shell.
- **14.** Characteristics of covalent compounds—(a) They are in all three physical states solid, liquid, or gas depending upon factors like molecular mass, van der Wall's force, covalency, Hydrogen bonding, polarity etc.

- (b) These are directional, soluble in less polar or non-polar solvents, less melting point and boiling point [than ionic compounds] due to weak van der-Waal forces, bad or good conductor of electricity.
- **15. Hybridization :** (a) Phenomenon of intermixing of atomic orbitals with slightly different energies to form new orbitals of equal energy and identical shape. The new orbitals are knows as **hybrid orbitals**.
 - (b) The number of hybrid orbitals is equal to number of atomic orbitals mixing.
 - (c) As the 's' character in hybrid orbital increases, electronegativity and size of hybrid orbital increases.

16. VSEPR (Valence shell electron pair repulsion theory):-

- (a) There are three types of repulsion in a covalent molecule lp lp > lp bp > bp bp.
- (b) These repulsion depend upon difference in electronegativity between combining atom.
- 17. Sigma and Pi π bond: (a) The bond formed by overlap of two atomic orbitals along the internuclear axis of two atoms is Sigma bonds.

Extent of overlap is large therefore strong bond.

- (b) π **bond**: The bond formed by sideways overlap of two atomic orbitals, extent of overlap is not along the nuclear axis therefore it is a weak bond.
- (c) A single bond contains σ bond; A double bond is one σ and one π bond a triple covalent bond contains one σ and 2π bonds.
- **18. Resonance :** (a) The delocalization of electrons in a molecule/ion which results in observed bond length, bond order, bond energy different from normal covalent bond data is known as resonance. Various resonating structures have nearly same energy and interconvertible to each other.
 - (b) It gives stability to the molecule/ion. Atom do not shift their position in any of the resonating structure. The structure which is near to all resonating structure and nearly explain the property of that molecule/ion is known

as resonating hybrid.

19. Dipole moment (μ): (a) For polar covalent molecules (atoms with difference in electronegativity] the product of charge present on either atom and distance b/w them is known as dipole moment. (b) Being vector quantity, if net resultant of all vector is zero the molecule has zero dipole moment and known as non polar molecule.

- **20. Hydrogen bonding :** The electrostatic interaction b/w molecules when H is bonded with highly electronegtive atoms (F, O, N only).
 - (a) **Intramolecular Hydrogen bonding :** Hydrogen bonding with in a molecule.
 - (b) Intermolecular hydrogen bonding: When hydrogen bonding is present between two same or different molecules.

- **21. Molecular orbital theory :** (a) The overlap of atomic orbitals of same symmetry of two homonuclear atoms to give addition or subtraction of wave functions and form bonding MO and antibonding MO respectively is known as MO theory.
 - (b) The e^- are filled in molecular orbitals in their increasing order of their energies in a molecule.
 - (c) Bond order:
 - $= \frac{\text{No. of electron in BMO} \text{No. of electrons in ABMO}}{2}$

- (d) More is bond order more is bond energy lesser is the bond length. If bond order zero then molecule/molecular ion do not exist.
- (e) Increasing order of energy of MO for upto $14e^-$ (For B₂, C₂ and N₂).

$$\sigma_{1s}, \sigma_{1s}, \sigma_{2s}, \sigma_{2s}, \sigma_{2s}, \pi_{2px} = \pi_{2py}, \sigma_{2pz}, \pi_{2px} = \pi_{2py}, \sigma_{2pz}$$

for other molecules $\to \sigma_{1s}$, σ_{1s} , σ_{2s} , σ_{2s} , σ_{2pz} , σ_{2px} = σ_{2py} , σ_{2px} = σ_{2py} , σ_{2pz}

- (d) This theory also decides the magnetic behaviour of molecules.
- **22.** Coordinate covalent bond: The sigma bond formed by donation of lp into vacant unhybridised orbital of other atom (acception atom) is known as coordinte covalent bond or donor acceptor or dative bond.

$$\ddot{N}H_3 + H^+ \rightarrow \begin{bmatrix} H \\ H - N - H \end{bmatrix}_{\stackrel{\cdot}{H}}^+ H - \ddot{O} + H^+ \rightarrow [H_3O]^+$$

$$H_2N \rightarrow BF_2$$

23. Bond strength; Bond energy; Bond length:

For covalent molecule Bond Enthalpy: $C \equiv C > C = C > C - C$

Bond Length :
$$C = C < C = C < C - C$$

Bond angles: (a) As the no. of lp increase; bp - lp, lp - lp repulsion increase therefore bond angles decrease.

(b) As lp decreases bond angle increases.

Important Points:

- **24.** (a) Maximum density of H₂O at 4°C due to extensive. Intermolecular hydrogen bonding.
 - (b) H₂O to H₂S bond angle decrease
 - (c) NH_3 more μ than NF_3 .
 - (d) NCl_3 more μ than NF_3 .
- 25. Van der waal forces weak intermolecular force of attraction.
 - (a) **Dipole dipole interactions** there which are present between polar molecules.
 - (b) **Dipole induced dipole interactions**. Those which are present polar between and non polar molecules.

- (c) Instantaneous dipole instantaneous induced dipole interaction (London force) dispersion forces: Those present between non-polar molecules.
- (d) Ion induced dipole interaction: Those which are present between ions and non-polar molecules.

1. What is the covalency of Al in AlCl₃?

[Ans. 3]

- 2. Out of MgCl₂ and NaCl which is more ionic?
- 3. Out of CCl₄ CHCl₃ and CH₂Cl₂, which is most polar.
- 4. Al₂O₃ has ionic or covalent bond.

[Ans. Ionic]

5. AlF₃ or AlCl₃, which is more covalent?

[Ans. AlCl₃]

6. What is the covalency of B in $[BF_4]^{1-}$?

[Ans. Four]

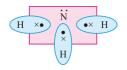
7. Ionic bonds are formed by metal with non-metals? (True/False)

[Ans. True]

8. Report covalency of 'N' in NH₃ and $^+_{NH_4}$.

[Ans. 3, 4]

- 9. Arrange HF, HCl and HBr in increasing order of their polarity.
- 10. Draw Lewis dot structure of CO.
- 11. Draw Lewis dot structure of NH₃.



- **12.** More is the number of resonating structures more is the stability of that molecule/ion. (True/False) [Ans. True]
- 13. Write O_2 , O_2^+ and O_2^- in their decreasing order of bond order.

[Ans.
$$(O_2^+ > O_2 > O_2^-]$$

14. Out of H_2^+ , H_2 which is more stable?

[Ans. H_2]

- **15.** Why dipole moment of BeCl₂ is zero.
- **16.** CO₂, BeCl₂, ICl₄⁻, SF₆ which has zero dipolemoment?

[Ans. All]

- 17. Determine the number of antibonding electrons in O_2^+ ? [Ans. 1]
- **18.** N_2 , O_2 , F_2 Arrange N_2 , O_2 and F_2 in decreasing order of their stability?

[Ans. $N_2 > O_2 > F_2$]

19. Which has zero dipole moment, CO₂ or SO₂?

[Ans. CO_2]

- 20. Dipole moment of hydrogen halides decreases from HF to HI. Why?
- **21.** Which out of the following does not show resonance CO_3^{2-} , BO_3^{3-} , SO_4^{2-} ?

[**Ans.** BO₃³⁻]

2 - Mark Questions

1. Which are isostructural species NO₂,CO₂, BeCl₂ and BCl₃?

[Ans. $\stackrel{^{+}}{NO}_2$; CO_2 , $BeCl_2$ all linear]

2. Out of the following BCl₃, H₂O, NO₃⁻ which have the same hybridization?

[Ans. BCl₃ NO₃⁻]

- 3. Which is angular or bent XeF_2 , H_2O , NO_2 ? [Ans. XeF_2 , NO_2]
- **4.** Which is not linear XeF_2 , NO_2 or CO_3^{2-} ? [Ans. CO_3^{2-}]
- 5. Which hydrocarbon is having most electronegative carbon atom?

(a) CH = CH (b) $CH_2 = CH_2$ (c) $CH_3 - CH_3$.

[Ans. a > b > c as 's' character increase EN increases]

6. $N(SiH_3)_3$ and $N(CH_3)_3$ are not isostructural justify?

[Ans. Si has vacant 'd' orbital 'C' does not]

7. Arrange the following in decreasing order of their bond angles.

CH₄, BeCl₂, NH₃.

 $[Ans. BeCl_2 > CH_4 > NH_3]$

- **8.** Hydrogen bond is shorter than H—H bond. (True/False) [Ans. True]
- 9. Which has nearly same bond angle?

NH₄⁺, CCl₄, CH₃

[Ans. NH_4^+ , CCl_4]

[Ans. (c)]

- 10. Which pair have different hybridization?
 - (a) $AlCl_3$; $[AlCl_4]^-$

(b) $BF_3; [BF_4]^-$

(c) NH₃, NH₄

- (d) NO₂, NO₂
- 11. KHF₂ exist but KHCl₂ KHBr₂ does not and why?

[Ans. (HF HF) Hydrogen bonding]

12. Why chlorine does not form hydrogen bonding whereas N does? .

[Ans. ∵ Cl has large size]

- 13. Which of the following molecules have sp^3 hybridized Be atom?
 - (a) $BeCl_2(g)$ (b) $BeCl_2$ (solid) (c) $BeCl_4^{2-}$. [Ans. $BeCl_2$ solid [$BeCl_4^{2-}$]
- **14.** Out of $[AlF_6]^{3-}$ and $[Al_2O_3]$, which have both covalent and ionic bond ? $[\mathbf{Ans.}\ AlF_6]^{3-}$
- **15.** Which have the shortest carbon-carbon bond length?
 - (a) Diamond (b) Benzene (c) Ethane (d) Cyclopropane [Ans. (b)]
- **16.** Which H₂O or HCl is not liquid and why?
- 17. Which is not see saw shaped?
 - (a) SF_4 (b) XeO_2F_2 (c) $XeOF_2$ (d) SCl_4 . [Ans. $XeOF_2$]
- **18.** Which is more stable, H_2^+ or \overline{H}_2 ? [Ans. H_2^+]
- 19. B₂ has ten electrons but paramagnetic why?
- **20.** Draw the resonating structure of \overline{NO}_2 .
- **21.** ClF₃ is bent T shaped but BF₃ is planar. Explain.
- 22. Density of ice is less than water. Why?
- **23.** o-Nitrophenol has less B.P. than *p*-nitrophenol. Why?
- **24.** (a) $H_2O + H^+ \rightarrow H_3O^+$ (b) $NH_3 + H^+ \rightarrow NH_4$. Out of (a) and (b), which is associated with change in hybridization, if any?
- **25.** Why do noble gas Ne₂ does not exist but Ne₂⁺ exists?
- **26.** H₂O is liquid at room temperature but H₂S is gas why?
- **27.** O_2 is paramagnetic but O_2^{2-} (peroxide ion) is diamagnetic why?
- 28. What is the difference between σ (sigma) and π (pi) bond explain diagrammatically?
- **29.** (a) F₂ and Cl₂, which has less bond dissocition energy and why?
 - (b) Out of O_2^+ , O_2^- which is more stable and why ?
- **30.** What is the difference between bond enthalpy and bond dissociation enthalpy?

- 1. Arrange in decreasing order of bond angle:
 - (a) H_2O , H_2S , H_2Se

$$[Ans. H_2O > H_2S > H_2Se]$$

(b) NO₂⁺, NO₂, NO₂⁻

[Ans.
$$\frac{NO_2 > NO_2 > NO_2^-}{(sp) (sp^2) (sp^2)}$$
]

(c) PF₃, PH₃, PCl₃

- $[\mathbf{Ans.}\ \mathsf{PCl}_3 > \mathsf{PF}_3 > \mathsf{PH}_3]$
- **2.** C₂ exists whereas Be₂ does not. Explain why?
- **3.** C₂H₄, C₂H₂, C₂H₆ arrange in decreasing order of :
 - (a) Bond length of C—C bond.
 - (b) Bond energy of C—C bond.
- **4.** Predict hybridization of carbon atoms in the compound $CH_3 CH = C = CH CH_3$
- **5.** What is the formula of compound and the _____.

Nature of bond formed beween element 'X' atomic no. 31 and element 'y' atomic number 8? Draw the Lewis dot structure. [Ans. X_2O_3]

- **6.** Which are odd electron molecules/ions : PCl_3 , NO, NO_2 , O_2^+ , O_2^- , O_2^- ?
- **7.** Write the bond angle in each of the following:

$$SO_4^{2-}CO_3^{2-}[H_3O]^+ \stackrel{-}{N}O_3 PCl_5 SF_4$$

- Write the number of electrons in valence shell of 'S' in (a) SF₆ (b) SO₂
 (c) SO₃. [Ans. 12, 10, 8]
- **9.** Arrange the following from strongest hydrogen bond to weakest hydrogen bond.
 - (a) H—F H—N

(b) H—O ... N—H

10. Give hybridization of following:

- 11. Explain the following:
 - (a) PH₃ is non polar PCl₃ is polar why?
 - (b) PCl₅ is non polar BF₄ is polar why?
 - (c) BCl₃ is non polar NCl₃ is polar why?
- 12. Five moles of σ bonds is present in simple hydrocarbon with sp^2 hybridization. Give formula of the compound.
- 13. Determine the formal charge of each 'O' atom, in O_3 .

- 1. Arrange the following in increasing order of property indicated:
 - (a) H₂O, NH₃, H₂S, HF

(Polar character)

(b) HF, HCl, HBr, HI

(Dipole moment)

(c) O_2 , O_2^+ , O_2^-

(Stability)

 $(d) NO_3^-, NO_2, NO$

('S' character of hybridization)

(e) BeCl₂, BCl₃, CCl₄, PCl₃

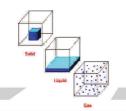
(Bond angle)

- 2. Which has:-
 - (a) Zero dipole moment CO₂; SO₂.
 - (b) sp hybridization SO₂, SO₃, or none.
 - (c) No octet rule OF₂, BCl₃, H₂Se.
 - (d) Zero bond order Ne₂, He₂, or both
 - (e) Paramagnetic character Cl⁻, Br, I⁻
- 3. Which has both (a) Polar and nonpolar bond H_2O_2 or BCl_3 .
 - (b) sp and sp^3 hybridization Propyne or Ethyne
 - (c) σ and π bonds and sp hybridization $CH_2 = C = CH_2$ or $CH_2 = CH$ — CH_3 .

- (d) Ionic and covalent bond, coordinate bonds: AgNO₃ AgF Ag₂SO₄.
- (e) Coordinate and only σ bond H_3O^+ ; $\stackrel{^{\top}}{N}H_4$; $\stackrel{^{\top}}{P}H_4$]
- **4.** (a) What is resonance hybrid? Explain its significance related to stability of compound.
 - (b) Draw resonating structures of benzene.
- 5. Why (a) BaSO₄ is insoluble although ionic in nature?
 - (b) ClF₃ has bent T-shape?
 - (c) SO₂ is angular but SO₃ is planar.
 - (d) NH, PH₃ have same hybridization but different bond angle?
 - (e) CuSO₄.5H₂O looses 4H₂O on heating but not fifth H₂O?
- **6.** Explain the scheme of hybridization in C_2H_4 , C_2H_6 and C_2H_2 .
- 7. Draw the resonating structures and resonance hybrid of following: CO_3^{2-} , NO_3^- , SO_3 , NO_2 and C_6H_6 .
- **8.** Draw the Lewis dot structure of (a) Al_2O_3 (b) Mg_3N_2 (c) CCl_4 (d) Na_2O_2 (e) NCl_3 .
- **9.** Draw the shapes of : BrF₃, XeF₄, NH₄⁺, ClF₅, XeF₆.
- 10. Arrange in increasing order of property indicated:
 - (a) HF, HCl, HBr, HI (thermal stability)
 - (b) LiF, LiCl, LiBr, LiI (ionic character)
 - (c) PH₃ PCl₃ (covalent character)
 - (d) $O_2 \rightarrow O_2^+$ (bond length)
 - (e) $N_2 \rightarrow N_2^+$ (bond order)
- 11. (a) Write the molecular orbital configuration of N₂. Calculate its bond order and predict its magnetic behaviour.
 - (b) Which out of NH₃ and NF₃ has higher dipolemoment and why?

- 12. (a) Describe the hybridisation in case of PCl_5 molecule (Atomic No. of P = 15)
 - (b) Why are axial bonds longer as compared to equatorial bonds in PCl₅ molecule?
 - (c) Which of the following has maximum bond angle?

$$\mathrm{H_2O,\,CO_2,\,NH_3\,\&\,CH_4}$$



Chapter - 5

States of Matter: Gases, Liquids and Solids

- On the basis of nature of intermolecular forces/molecular interactions, matter exists in three physical states: solid, liquid and gas.
- Intermolecular forces are the forces of attraction or repulsion between interacting particles (atoms and molecules). Attractive/repulsive intermolecular forces are known as van der Waal's forces.

Different types of van der Waal's forces are:

- (a) **Disperson forces or London forces:** The interaction which is present between two non polar molecules for example force between: noble gases.
- (b) **Dipole-dipole forces**: The interaction which is present between molecules having permanent dipoles *i.e.*, between polar molecules, for example NH₃, HCl etc.
- (c) **Dipole-induced dipole forces**: The interaction which is present between a polar and non polar molecule.
- **Boyle's law:** At constant temperature, the pressure of a fixed amount of gas, varies inversly with volume.

$$P \qquad \alpha \frac{1}{V}$$

$$P_1V_1 = P_2V_2$$
 [At constant temperature]

• Charle's law: At constant pressure, the volume of a fixed mass of gas is directly proportional to its absolute temperature.

$$V \alpha T$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
 [At constant pressure (p) and n]



• **Gay Lussac's law:** At constant volume, pressure of a fixed amount of gas varies directly with the absolute temperature.

$$P \propto T$$
, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ [At constant volume (V) and n].

• STP (Standard Temperature and Pressure): STP means 273.15 K (0°C) temperature and 1 bar (*i.e.*, exactly 10^5 Pascal.) Volume occupied by 1 mole gas at STP = 22.7 L.

If pressure is taken in atm (atmosphere), then the standard molar volume is 22.4 L.

• Ideal gas equation : PV = nRT

R is universal gas constant.

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$$

- Combined gas law: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
- Density and molar mass of a gaseous substance :

$$\mathbf{M} = \frac{d\mathbf{R}\mathbf{T}}{\mathbf{P}}$$

• **Dalton's law of partial pressure :** Dalton states that the total pressure exerted by the mixture of non reacting gases is equal to the sum of the partial pressures of individual gases.

$$P_{total} = P_1 + P_2 + P_3 +$$
 [at constant T, V]

$$P_1 = x_1 \times P_{Total} = Here x_1$$
 is called mole fraction of the first gas.

$$P_{dry gas} = P_{Total} - Aqueous tension.$$

Here aqueous tension is the pressure exerted by water vapours.

• Compressibility factor: The extent of deviation of a real gas from an ideal behaviour is expressed in terms of compressibility factor, $Z = \frac{PV}{nRT}$

For ideal gas, Z=1 at all temperatures and pressures. For real gases, greater is the deviation in the value of Z from 1, more is the deviation from ideal behaviour. When Z < 1, the gas is said to show negative deviation. This implies that gas is more compressible then expected from ideal behaviour. When Z > 1, the gas is said to show positive deviation and the gas is less compressible than expected from ideal behaviour.

At ordinary temperatures (T \geq 273 K), only H₂ and He show positive deviations. However at low temperatures, even these gases show negative deviation *i.e.*, < 1. *For example*, in case of these gases, if T << 273 K, Z < 1.

- Boyle temperature: The temperature at which a real gas behaves like an
 ideal gas over an appreciable pressure range is called Boyle temperature
 or Boyle point.
- Causes of deviation from ideal behaviour: The following two assumptions of the kinetic theory of gases are faulty:
 - (a) The volume occupied by the gas molecules is negligible as compared to the total volume of the gas.
 - (b) The forces of attraction or repulsion between the gas molecules are negligible.

The above assumptions are correct only if the temperature is high and pressure is low.

van der Waal's equation:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$
 for 1 mole of the gas

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad \text{for } n \text{ moles of the gas}$$

Here a and b are constants called van der Waal's constants.

• Significance and units of van der Waal's constants: 'a' gives the idea of the magnitude of attractive forces among the gas molecules. As correction

in pressure is
$$P = \frac{an^2}{V^2}$$
, therefore $a = (P \times V^2)/n^2 = atm L^2 mol^2$.

As correction in volume V = nb, therefore 'b' has the unit of L mol⁻¹. The near constancy in the volume of b shows that the gas molecules are incompressible.

- **Vapour pressure :** The pressure exerted by the vapours of a liquid, when it is in equilibrium with the liquid surface, at constant temperature.
- **Boiling temperature :** The temperature at which vapour pressure of a liquid is equal to the external pressure.
- At 1 atm, boiling temperature is called normal boiling point.
- At 1 bar boiling temperature is called standard boiling point.

- Vapour pressure of a pure liquid depends upon (i) intermolecular forces, (ii) Temperature.
- Surface tension is defined as force acting per unit length perpendicular to the line drawn on the surface. Its units is Nm⁻¹.
- Effect of temperature on surface tension: Surface tension decreases with increase in temperature with the increase in temperature, kinetic energy of molecules increases. As a result, intermolecular forces decreases and hence force acting per unit length decreases.
- **Viscosity**: It is defined as resistance offered to the flow of liquid due to internal friction between layers of fluids as they pass over each other.

$$F = \eta A. \frac{du}{dx}$$

η is called **coefficient of viscosity.**

Effect of temperature on viscosity : Viscosity decrease with increase in temperature because with the increase in temperature the average kinetic energy increases and the intermolecular forces can be easily overcome.

The Solid State

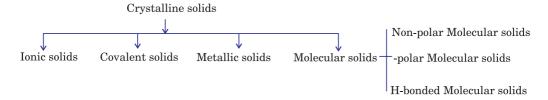
Crystalline and Amorphous solids

	Crystalline solids	Amorphous solids
1.	They have regular geometry	They have irregular geometry
2.	They have long range order	They have short range order.
3.	They have sharp melting point.	They have no sharp melting point.
4.	They are anisotropic	They are isotropic
5.	They give clean and smooth surface on cleavage.	They give irregular cut on cleavage
6.	They have definite heat of fusion.	They do not have definite heat of fusion.
7.	They are true solids.	They are pseudo solids or super cooled liquids.

Anisotropic : Solids which have different values of their physical properties such as refractive index, conductivity etc. in different directions.

Isotropic: Solids which have same values of their physical properties such as refractive index, conductivity etc. in different directions.

Classification of crystalline solids:



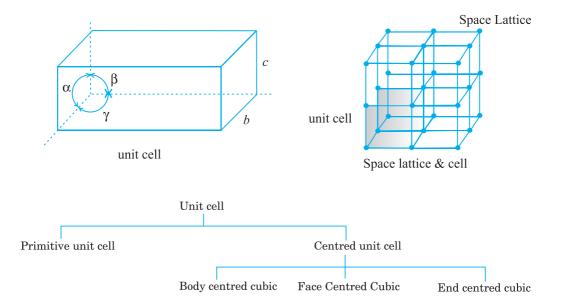
Space lattice (Crystal lattice)

A regular arrangement of the constituents particles (atoms, molecules or ions) in the three dimensional space which represent the geometry of a crystal is called space lattice.

There are only 14 possible three dimensional lattices. These are called **Bravias lattices**

Unit cell

The smallest repeating unit of the space lattice is called unit cell.



Total number of atoms (Particle) per unit cell (Z)

Unit cell	Contributions	Number of particles (Z)
Simple cubic	$(1/8 \times 8) = 1$ atom (corner)	1
Body centred cubic	$(1/8 \times 8) = 1$ atom (corner)	2
	$(1 \times 1) = 1$ atom (Body centre)	
Face centred cubic	$(1/8 \times 8) = 1$ atom (corner)	4
	$(1/2 \times 6) = 3$ atom (face centre)	

Close packing

Close packing in one dimensions

In this arrangement, each sphere is in contact with two of its neighbours.



Close packing of spheres in one dimensional

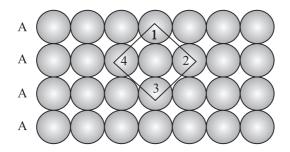
Close packing in two dimension

Square close packing

In this arrangement each sphere is in contact with four of its neighbours, thus packing is called square close packing.

Coordination number is **four**.

52.4% of the available space is occupied by the spheres (AAA type arrangement).



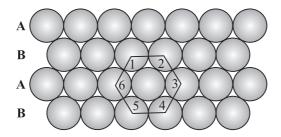
Square close packed layer

Hexagonal close packing

In this arrangement each sphere is in contact with six of its neighbours, thus packing is called Hexagonal close packing.

Coordination number is six.

60.4% of the available space is occupied by the spheres (ABAB type arrangement).



Close packing in three dimensional

HCP and CCP have equal efficiency i.e 74% of the space is occupied and coordination number is 12. CCp arrangement has FCC lattice.

Unoccupied spaces in solids are called **interstitial voids** or **interstitial sites**.

Two types of interstitial voids are:

(i) Tetrahedral void

(ii) Octahedral void

Number of tetrahedral voids = 2 N

(where N is number of close packed particles)

Number of octahedral voids = N

Type of unit cell	Relarion between r , a , & d	Packing fraction
Simple cubic	r = a/2	52.4%
Body centred cubic	$d = \frac{\sqrt{3}a}{2} r = \frac{a}{2\sqrt{2}}$	68%
Face centred cubid	$d = \frac{a}{\sqrt{2}} r = \frac{a}{2\sqrt{2}}$	74%

r = radius of the atom, d = nearest neighbour distance between two atoms & a = edge length of unit cell.



Packing Efficiency (Packing fraction)

The percentage of the total space which is occupied by the particles in a certain packing is known as packing efficiency or the total spacefilled is called **packing fraction.**

Packing efficiency =
$$\frac{\text{Number of atoms in unit cell} \quad \text{Volume of one atom}}{\text{Volume of the cubic unit cell}}$$

Density of the unit cell

Density of the unit cell =
$$\frac{Z \times M(g)}{a^3 \times N_A}$$

where Z is the number of atoms per unit cell, M is molar mass / atomic mass, a is the edge length of the cubic unit cell and $N_{\rm A}$ is the Avogadro constant

Imperfection or Defects in solids

Any deviation from perfectly ordered arrangement of atoms in crystal is called imperfection or defect. There are two types of the defects: (i) Line defects (ii) point defects.

(i) Line defects

The defects which arise due to irregularity or deviation from ideal arrangement in entire row of lattice points.

(ii) Point defects

The defects which arise due to irregularity in the arrangement of atoms or ions are called atomic imperfection or point defect.

Point defects can be classified in to three types

(a) stoichiometric defect

(b) Non stoichiometric defect

- (c) Impurity defect
- (a) stoichiometric defect (i) vacancy defect: When some of the lattice sites are vacant in a crystal, the crystal is said to have vacancy defect.
- (ii) Interstitial defect: When some constituent particles occupy an interstitial site the crystal is said to have interstitial defect.

(iii) Schottky defect: It is basically a vacancy defect in ionic solids

In this defect equal number of cations and anions are missing from their lattice site so that the electrical neutrality is maintained.

Conditions causing Schottky defects:

- (i) high coordination number, and
- (ii) small difference in the size of cations and anions

For example, NaCl, KCl, KBr

(iv) Frenkel defect

In this defect, the smaller ion (usually cation) is dislocated from its normal site to an interstitial site.

It creates a vacancy defect at its original site and an interstitial defect at its new location. Frenkel defect is also called dislocation defect.

Conditions causing Frenkel defects:

This type of defect is generally occurs in compounds which have

- (i) low coordination number, and
- (ii) large difference in the size of cations and anions.

Frenkel defects are found in silver halides (AgCl, AgBr and AgI)

(b) Non stoichiometric defects

Theses defect are of the two types:-

(a) Metal excess defect:

(i) Metal excess defect due to anion vacancies:

In this case, negative ions may be missing from their lattices leaving holes in which the electron remain entrapped to maintain the electrical neutrality. The anionic sites occupied by unpaired electrons are called F-centres.

(ii) Metal excess due to the presence of extra cations at interstitial sites:

In this case, there are extra positive ions occupying interstitial sites and electrons in another interstitial sites to maintain electrical neutrality.

(b) Metal deficiency defect

In this defect, the positive ions may be missing from their lattice sites. The extra negative charge may be balanced by some nearby metal ion acquiring extra positive charges.

(c) Impurity defect (Due to ions)

The process of adding impurities to a crystalline substance so as to change its properties is called doping

p -type semiconductors

Group-14 group elements doped with group-13 are called p-type semiconductors because group 13 elements like B, A1 or Ga contains three valence electrons.

n-type semiconductors:

When group 14 elements (Si or Ge) are doped with group 15 elements like P or As,

Magnetic properties:

Diamagnetic substances (Diamagnetism.)

The substances which are weakly repelled by the external magnetic field are called diamagnetic substances, e.g. TiO, H, 0, NaCl, benzene, etc.

Paramagnetic substances

The substances which are weakly attracted by external magnetic field are called paramagnetic substances.

Ferromagnetic substances (Ferromagnetism):-

The substances which are strongly attracted by a magnetic field are called ferromagnetic substances. For ex:- Fe, Ni, Co, CrO₂

Antiferromagnetic substances (Antiferromagnetism):

The substances which have net magnetic moments zero due to equal and opposite allignment of domains.

Examples are MnO, FeO, CoO, NiO and many other oxides.

Ferrimagnetic substances (Ferrimagnetism):

Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers. Ferromagnetism (a)

Antiferromagnetism (b)

Ferrimagnetism (c)

1 - Mark Questions

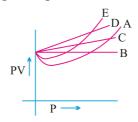
- 1. Name the intermolecular forces, which include the term. van der Waal's forces. [Ans. LONDON forces, Dipole-Dipole, Dipole-induced dipole]
- 2. Define Boyle's law.
- **3.** Write the condition in terms of temperature and pressure, under which all gases obey Charle's law. [Ans. High temperature, low pressure]
- 4. Mention the volume occupied by one mole of an ideal gas at STP.

[Ans. 22.7 L]

5. Define the term absolute zero.

[Ans. 0K]

- **6.** Define aqueous tension.
- 7. Mention the S.I. unit for the quantity $\frac{PV^2T^2}{n^2}$. [Ans. Nm⁴ K² mol⁻¹]
- **8.** Define the term critical temperature.
- 9. Write any two postulates of kinetic molecular theory of gases.
- 10. Which curve in the figure represents the curve for ideal gas? [Ans. B]



- 11. Define the term normal boiling point of a liquid.
- 12. Mention the factors on, which the vapour pressure of a pure liquid depends?
- 13. Define surface tenstion.
- 14. What do you understand by the term viscosity?

- **15.** Out of Ethyl alcohol or Dimethyl lether, which one have higher vapour pressure at same temperature? [Ans. Dimethylether]
- **16.** Why glass is called supercooled liquid?

[Hint: Its molecules move under gravity.]

- 17. Why glass planes fixed to windows or doors of old buildings are found be thicker at the bottom?
- **18.** Some of the glass objects from ancient civilizations are found to be milky in appearance. Explain.

[Hint: Reallignment of molecules takes place due to movement because of constant heating and cooling]

- **19.** "Crystalline solids are anisotropic in nature" what does this statement mean?
- **20.** What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass?

[Hint: On melting quartz and then rapidly cooling it.]

- 21. Write a feature which will distinguish a metallic solid from ionic solid.
- **22.** Name the crystal system for which all four types of unit cells are possible. [Hint: Orthorhombic]
- 23. What is the total number of atoms per unit cell in a FCC crystal structure?
- **24.** What difference in behaviour between the glass and sodium chloride would you expect to observe,if you break off a piece of either cube?
- **25.** Give the significance of a lattice point.
- 26. What type of stochiometric defect is shown by (i) ZnS and (ii) CsCl?
- **27.** If the formula of a compound is A₂B, which sites would be occupied by A ions?

[Hint: A ions occupy tetrahedral voids]

28. How many octahedral voids are there in 1 mole of a compound having cubic closed packed structure?

- **29.** Calculate the number of atoms in a cubic unit cell having one atom on each corner and two atoms on each body diagonal.
- **30.** In NaCl crystal, Cl⁻ ions form the cubic close packing. What sites are occupied by Na⁺ ions?
- **31.** In Corrundum, O²⁻ ions from hep and Al³⁺ occupy two third of octahedral voids. Determine the formula of corrundum.
- **32.** Why is Frenkel defect not found in pure alkali metal halides?
- **33.** What is the formula of a compound in which element Y forms ccp lattice and atoms X occupy 1/3rd of tetrahedral voids?
- **34.** Although pure silicon is an insulator then how does it behave as a semiconductor on heating?
- **35.** Name the crystal defect which lowers the density of an ionic crystal.
- **36.** What makes the crystal of KCl sometimes appear violet?
- **37.** Which point defect in ionic crystal does not alter the density of the relevant solid?
- **38.** Name one solid in which both Frenkel and Schottky defects occur.
- **39.** Fe₃O₄ is ferrimagnetic at room temperature but becomes paramagnetic at 850 K. Why?
- **40.** Why common salt is some time yellow instead of being pure white?
- **41.** Why conductivity of the metal decrease with increase in temperature?
- **42.** What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic?
- **43.** What type of magnetism is shown by a substance if magnetic moments of domains are arranged in the same direction?

2 - Marks Questions

- 1. What will be the minimum pressure required to compress $500 dm^3$ of air at 1 bar to $200 dm^3$ at 30° C? [Ans. 2.5 bar]
- 2. Name the intermolecular force present in:
 - (i) H₂O (ii) HCl

[Ans. H-bonding, Dipole-Dipole]



- 3. Explain Avogadro's law.
- **4.** Find the molar mass of a gas if 300 mL of this has mass of 0.368 g at STP. [Ans. 27.84 g/mol]
- **5.** Why do real gases show deviation from ideal behaviour? Write van der Waal's equation for *n* moles of a gas.
- 6. Calculate the temperature of 4 mole of a gas occupying in 5 dm^3 at 3.32 bar. (R = 0.083 bar dm^3 K⁻¹ mol⁻¹) [Ans. 50K]
- 7. Calculate the volume occupied by 8.8 g of CO_2 at 31.1°C and 1 bar pressure. [R = 0.83 bar LK⁻¹ mol⁻¹] [Ans. 5.05 L]
- **8.** Explain the physical significance of van der Waal's parameter.
- **9.** Compressibility factor 'Z' of a gas is given as $Z = \frac{PV}{nRT}$.
 - (i) What is the value of Z for an ideal gas?
 - (ii) For real gas, what will be the effect on value of Z above Boyle temperature? [Ans. Z = 1, Z > 1]
- **10.** At 25°C and 760 mm Hg pressure a gas occupies 600 mL volume. What will be its pressure at a height where temperature is 10°C and volume of the gas is 640 mL.

 [Ans. 676.6 mm Hg]
- 11. Define the terms:
 - (i) Standard boiling point.
 - (ii) Vapour pressure of a liquid.
- **12.** Drops of liquid are spherical in nature. Explain. Mention the effect of temperature on surface tension.
- 13. Write the S.I. units of:
 - (i) Surface tension.
 - (ii) Coefficient of viscosity.
- **14.** Define viscosity. Mention the effect of temperature and pressure on viscosity of a liquid.

15. Explain:

- (i) Liquid drops are spherical in shape, why?
- (ii) Liquid tends to rise in a capillary.
- **16.** List four distinctions between crystalline and amorphous solids with one example of each.
- 17. Give suitable reason for, the following-
 - (a) Ionic solids are hard and brittle (b) Copper is malleable and ductile
- 18. Explain:
 - (a) List two differences between metallic and ionic crystals.
 - (b) Sodium chloride is hard but sodium metal is soft.
- 19. What do you understand by the following types of stacking sequences:
 - (a) ABAB......(b) ABCABC......
- **20.** What kind of lattices do these sequences lead to?
- **21.** Calculate the number of atoms in a cubic based unit cell having one atom on each corner and two atoms on each body diagonal.
- 22. A unit cell consists of a cube in which there are A atoms are at the corners and B atoms at the face centres. Two A atoms are m issing from the two corners of the unit cell. What is the formula of this compound?
- **23.** Pure silicon is an insulator. Silicon doped with phosphorus is a semiconductor. Silicon doper with gallium is also a semiconductor. What is the difference between the two types?
- **24.** Explain how vacancies are introduced in a solid NaCl crystal when a compound containing cation of higher valence is added to it?
- **25.** What is meant by non-stoichiometric defect? Ionic solids which have anionic vacancies due to metal excess defect develop colour. Explain with the help of suitable example.
- **26.** Define the term 'point defects'. Mention the main difference between stoichiometric and non-stoichiometric point defects.
- 27. In a crystalline solid, anions B are arranged in a cubic close packing. Cations A are equally distributed between octahedral and tetrahedral voids. If all the octahedral voids are occupied, What is the formula of the solid?

- **28.** In a solid, oxide ions are arranged in ccp.one sixth of the tetrahedral voids are occupied by the cations A while one third of the octahedral voids are occupied by the cation B. What is the formula of the compound?
- **29.** In the mineral, spinel having the formula MgAl₂O₂ oxide ions are arranged in the cubic close packing, Mg²⁺ ions occupy tetrahedral voids and Al³⁺ ions occupy the octahedral voids.
 - (i) What percentage of tetrahedral voids is occupied by Mg²⁺ ions?
 - (ii) What percentage of octahedral voids is occupied by Al³⁺ ions?
- **30.** The electrical conductivity of a metal decrease with rise in temperature while that of a semiconductor increase. Explain
- **31.** CdCl₂, will introduce impurity defect if added to AgCl crystal. Explain.
- **32.** In a crystalline solid, the atoms A and B are arranged as follows:
 - (a) Atoms A are arranged in ccp array.
 - (b) Atoms B occupy all the octahedral voids and half of tetrahedral voids. What is the formula of the compound?
- **33.** Nickel oxide has formula $Ni_{0.94}O_{1.00}$. What fractions of the nickel exist as Ni^{2+} and Ni^{3+} ions?
- **34.** The composition of a sample of wustite is $Fe_{0.93}O_{1.00}$. What percent of iron is present in the form of Fe(III)?
- **35.** Tungsten crystallizes in body centred cubic unit cell. If the edge length of the unit cell is 316.5 pm, what is the radius of tungsten atom?

[**Ans:** 137 Pm]

3 - Mark Ouestions

- 1. Define and explain Dalton's Law of partial pressure.
- 2. A balloon is filled with hydrogen at room temperature. It will burst if pressure exceeds 0.2 bar. If at 1 bar pressure the gas occupies 2.27 L volume, upto what volume can the balloon be expanded?

[**Ans.** 11.35 L]

3. Calculate the total pressure in a mixture of 8g of dioxygen and 4g of dihydrogen confined in a vessel of 1dm³ at 27°C.

 $[R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}]$

[**Ans.** 56.025 bar]

- **4.** 300 mL of oxygen gas at -10° C are heated to 10° C. Find the volume of gas at 10° C if pressure remains constant. [Ans. 322.8 mL]
- 5. A gas at a pressure of 5 atm is heated from 0° to 546°C and is simultaneously compressed to one third of its original volume. Find the final pressure of the gas.

 [Ans. 45 atm]
- 6. Pressure of one gram of an ideal gas A at 27°C is found to be 2 bar. When 2g of another gas (ideal) B is introduced in the same flask at the same temperature the pressure becomes 3 bar. Find a relationship between their molecular masses.

 [Ans. $M_{\rm R} = 4M_{\rm A}$]
- 7. What will be the pressure exerted by a mixture of 3.2g of methane and 4.4 g of carbon dioxide contained in a 9 dm³ flask at 27°C.

[**Ans.** 0.82 atm]

- **8.** A neon-dioxygen mixture contains 70.6 dioxygen and 167.5 neon. If the pressure of the mixture of gases in cylinder is 25 bar. What is the partial pressure of dioxygen and neon in the mixture. [Ans. 5.25 bar, 17.75 bar]
- 9. With the help of a gas laws, deduce an expression for the ideal gas equation. What is the utility of the gas equation?
- 10. A vessel of 120 mL capacity contains a certain mass of a gas at 20°C and 750 mm Hg pressure the gas was transferred to a vessel whose volume is 180 mL. Calculate the pressure of the gas at 20°C. [Ans. 500 mm Hg]

11. Explain:

- (i) Liquid at higher altitudes boil at low temperature.
- (ii) In hospital surgical instruments are sterlised in auto caves.
- (iii) Out of, alcohols and ethers of comparable mass which one have higher boiling points?
- **12.** (i) Define surface energy in relation to surface tension.
 - (ii) Name the temperature at which the density of water is maximum.
 - (iii) Moist soil grains are pulled together. Explain.
- **13.** (i) Define the term coefficient of viscosity. Name the unit of viscosity coefficient in cgs system.
 - (ii) Give the difference between boiling and evaporation.
- **14.** Explain with suitable reason:
 - (i) Tea or coffee is sipped from the saucer, when it is quite hot.
 - (ii) Liquids posseses fluidity.

- **15.** Which among the following will have?
 - (i) HCl or H₂O (Higher boiling point)
 - (ii) Ether or water (Higher viscosity)
 - (iii) $Br_2(l)$ or water (Lower surface tension)
- 16. Write the relationship between atomic radius (r) and edge length (a) of cubic unit cell for

 - (a) Simple cubic unit cell (b) Body centred cubic unit cell
 - (c) Face centred cubic unit cell
- 17. Write and explain three differences between Schottky and Frenkel defects under the heads:
 - (i) Effect on density
- (ii) Effect on electrical conductivity
- (iii) Effect on stability of the crystal
- 18. What is a semiconductor? Describe the two main types of semiconductors on the basis of their conductance mechanism.
- **19.** Explain the following with one examples each:
 - (a) Ferromagnetism
- (b) Antiferromagnetism
- (c) 13-15 compounds
- **20.** Explain the following terms with suitable examples :
 - (a) Ferrimagnetism
- (b) *n*-type semiconductor
- (c) Forbidden zone
- 21. How would you account for the following:
 - (i) Frenkel defects are not found in alkali metals.
 - (ii) Schottky defects lower the density of the related solid.
 - (iii) Impurity doped silicon is a semiconductor.
- 22. (a) What type of semiconductor is obtained when silicon is doped with boron?
 - (b) What type of magnetism is shown in the following alignment of magnetic moments?



- (c) What type of defect is produced when AgCl is doped with CdCl₂? Answer the following questions:
- 22. (i) What type of stoichiometric defect shown by the crystal?
 - (ii) How is the density of the crystal affected by this defect?
 - (iii) What type of ionic substances show such defect?

$$A^{+}$$
 B^{-} A^{+} B^{-} A^{-} B^{-} A^{-} B^{-} A^{-} B^{-} A^{-} B^{-}

- **24.** (a) A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?
 - (b) Atoms of element B form *hcp* lattice and those of the element A occupy 2/3rd of tetrahedral voids. What is the formula of the compound formed by the elements A and B?
- **25.** An element crystallises in a cubic close packed structure having a fcc unit cell of an edge 200 pm. Calculate the density if 200 g of this element contain 24×10^{23} atoms. [Ans.: 41.6 g cm^{-3}]
- **26.** A fcc unit cell containing atoms of element (molar mass 60.4 g mol^{-1}) has cell edge 4×10^{-8} cm. Calculate the density of unit cell.

[Ans.:
$$6.23 \text{ g/cm}^3$$
]

- **27.** KF has NaCl structure. It's density is 2.48 g/cm^3 . Calculate edge length of crystal lattice. (Given At. mass of K = 39 g mol⁻¹, F= 19 g mol⁻¹ and $N_A = 6.002 \times 10^{23} \text{ mol}^{-1}$) [Ans.: 538 pm]
- 28. Molybednum has atomic mass 96 g mol $^{-1}$ with density 10.3 g/cm 3 . The edge length of unit cell is 314 pm. Determine lattice structure whether simple cubic, fcc or bcc. (Given $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$)

[Ans.:
$$Z = 2$$
, bee type]

29. Iron has a bcc unit cell with a cell edge of 286.65 pm. The density of iron is 7.87 g cm^{-3} . Use this information to calculate Avogadro's number (At. Mass of Fe = 56 g mol^{-1})

[Ans.:
$$6.022 \times 10^{23} \text{ mol}^{-1}$$
]

30. The density of copper metal is 8.95 g cm⁻³. If the radius of copper atom is 127 pm, is the copper unit cell a simple cubic, a body-centred cubic or a face centred cubic structure?

(Given at. mass of Cu = 63.54 g mol⁻¹ and
$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$
]

[Ans.: $Z = 4$, fcc type]

31. The well known mineral fluorite is chemically calcium fluoride. It is known that in one unit cell of this mineral there are 4 Ca^{2+} ions and $8F^{-}$ ions and that Ca^{2+} ions are arranged in a fee lattice. The F^{-} ions fill all the tetrahedral holes in the fcc lattice of Ca^{2+} ions. The edge of the unit cell is 5.46×10^{-8} cm in length.

The density of the solid is $3.18~{\rm g~cm^{-3}}$. Use this information to calculate Avogadro's number (Molar mass of CaF₂ = $78.08~{\rm g~mol^{-1}}$).

[Ans.:
$$6.02 \times 10^{23} \text{ mol}^{-1}$$
]

32. Silver crystallizes in face centred cubic unit cell. Each side of this unit cell has a length of 400 pm.Calculate the radius of the silver atom. (Assume the atoms just touch each other on the diagonal across the face of the unit cell. That is each face atom is touching the four corner atoms.)

- **33.** The density of the lead is 11.35 g cm⁻³ and the metal crystallizes with fcc unit cell. Estimate the radius of the lead atom. [Ans: 175 pm]
- **34.** An element with density 11.2 g cm⁻³ forms a f.c.c lattice with edge length of 4×10^{-8} cm. Calculate the atomic mass of the element.

- **35.** An element with molar mass 27 g mol^{-1} forms a cubic unit cell with edge length 4.05×10^{-8} cm. If its density is 2.7 g cm^{-3} , what is the nature of the cubic unit cell? [Ans: FCC]
- **36.** An element crystallizes in a fcc lattice with cell edge of 250 pm. Calculate the density if 300 g of this element contain 2×10^{24} atoms. [38.4 g/cm^3]
- **37.** An element 'X' (At. mass = 40 g mol⁻¹) having FCC structure, has unit cell edge length of 400 pm. Calculate the density of 'X' and the number of unit cell in 4g of 'X'

$$[d = 4.15 \text{ g/cm}^3, \text{ No. of unit cell} = 1.5 \times 10^{22}]$$

5 - Mark Questions

- 1. (a) An element has atomic mass 93 g mol⁻¹. If the edge length of its unit cell is 300 pm, identify the type of unit cell. [Ans.: BCC, Z = 2]
 - (b) Write any two differences between amorphous solids and crystalline solids.
- (a) Calculate the number of unit cells in 8.1 g of aluminium, if it crystallizes in a f.c.c. structure. (Given: Atomic mass of Al = 27 g mol⁻¹)
 [Ans: No. of unit cell 4.5 × 10²²]
 - (b) Give reasons:
 - (i) In stoichiometric defects, NaCl exhibits schotky defect and not Frenkel defect.
 - (ii) Silicon on doping with Phosphorus forms n-type semiconductor.
 - (iii) Ferrimagnetic substances show better magnetism than antiferromagnetic substance.
- 3. (a) An element crystallises in b.c.c. lattice with cell edge of 400 pm. Calculate its density if 500 g of this element contains 2.5×10^{24} atoms. [Ans: 6.25 g/cm^3]
 - (b) A metallic element crystallises into a lattice having a pattern of ABAB...... and packing of spheres leaves out voids in the lattice. What type of structure is formed by this arrangement?

[Ans: HCP]

- 4. Mention the intermolecular forces present between:
 - (a) $\rm H_2O$ and alcohol (b) $\rm Cl_2$ and $\rm CCl_4$ (c) He and He atoms (d) $\rm Na^+$ ion and $\rm H_2O$ (e) HBr and HBr.
- 5. (a) Find the pressure of 4g of O₂ and 2g of H₂ confined in a bulb of 1 litre at 0°C.
 - (b) What is the molar volume of a gas at SATP conditions?
 - (c) Define and explain Gay Lussac's law.
- **6.** (a) For Dalton's law of pressure derive the expression $P_{gas} = X_{gas} P_{total}$.
 - (b) A 2-L flask contains 1.6 g of methane and 0.5 g of hydrogen at 27°C. Calculate the partial pressure of each gas in the mixture and also, calculate the total pressure.

[Ans. $pCH_4 = 1.23$ atm, $pH_2 = 3.079$ atm, $P_{total} = 4.31$ atm.]

7. (a) Using van der waal's equation calculate the constant 'a' when two moles of a gas confined in a four litre flask exerts a pressure of 11.0 atm. at a temperature of 300 K. The value of 'b' is 0.05 litre mol⁻¹.

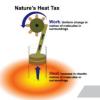
[Ans. 6.49 atm $L^2 \text{ mol}^{-2}$]

- **8.** (a) Mention the factors on which vapour pressure of a pure liquid depends.
 - (b) Define boiling point of a liquid.
 - (c) Which will have higher viscosity Glycerol or Ethylene glycol?

[Ans. Glycerol]

(d) Surface tension of a liquid with increase in the magnitude of intermolecular forces. [Ans. Increases]





Chapter - 6

Chemical **Thermodynamic**

- **System :** Specific part of universe in which thermodynamic observations are made.
- **Surroundings**: Everything which surrounds the system.
- Types of the System :
 - (i) **Open System:** Exchange both matter and energy with the surroundings. For example: Reactants in an open test tube.
 - (ii) **Closed System:** Exchange energy but no matter with the surroundings. For example: Reactants in a closed vessel.
 - (iii) **Isolated System:** Neither exchange energy nor matter with the surroundings. For example: Reactants in a thermos flask. No system is perfectly isolated.

• Thermodynamic Processes:

- (i) Isothermal process : $\Delta T = 0$
- (ii) Adiabatic process : $\Delta q = 0$
- (iii) Isobaric process : $\Delta P = 0$
- (iv) Isochoric process : $\Delta V = 0$
- (v) Cyclic process : $\Delta U = 0$
- (vi) Reversible process: Process which proceeds infinitely slowly by a series of equilibrium steps.
- (vii)Irreversible process: Process which proceeds rapidly and the system does not have chance to achieve equilibrium.
- Extensive Properties: Properties which depend upon the quantity or size of matter present in the system. For example: mass, volume, internal energy, enthalpy, heat capacity, work etc.

- Intensive Properties: Properties which do not depend upon the quantity or size of matter present in the system. For example: temperature, density, pressure, surface tension, viscosity, refractive index, boiling point, melting point etc.
- **State Functions:** The variables of functions whose value depend only on the state of a system or they are path independent. For example: pressure (P), volume (V), temperature (T), enthalpy (H), free energy (G), internal energy (U), entropy (S), etc.
- Internal Energy (U): It is the sum of all kind of energies possessed by the system.
- First Law of Thermodynamics: "The energy of an isolated system is constant."

Mathematical Form : $\Delta U = q + w$

- Sign Conventions for Heat (q) and Work (w):
 - (i) W = + ve, if work is done on system
 - (ii) W = -ve, if work is done by system
 - (iii) q = + ve, if heat is absorbed by the system
 - (iv) q = ve, if heat is evolved by the system
- Work of Expansion/compression : $w = -P_{ext}(V_f V_i)$
- Work done in Isothermal Reversible Expansion of an Ideal Gas:

$$w_{rev} = -2.303 nRT \log \frac{V_f}{V_i}$$

Or,
$$w_{rev} = -2.303 nRT \log \frac{P_i}{P_f}$$

- Significance of ΔH and ΔU : $\Delta H = q_p$ and $\Delta U = q_v$
- Relation between $\Delta \mathbf{H}$ and $\Delta \mathbf{U}$: $\Delta \mathbf{H} = \Delta \mathbf{U} + (n_p n_r) \mathbf{R} \mathbf{T}$ for gaseous reaction.
 - (i) $\Delta H = \Delta U$ if $(n_p n_r)$ is zero; e.g., $H_2(g) + I_2(g) \rightarrow 2HI(g)$
 - (ii) $\Delta H > \Delta U$ if $(n_n n_r)$ is positive; e.g., $PC1_5(g) \rightarrow PC1_3(g) + C1_2(g)$
 - (iii) $\Delta H < \Delta U$ if $(n_p n_r)$ is negative; e.g., $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
- **Heat capacity (C):** Amount of heat required to raise the temperature of a substance by 1°C or 1 K.

$$q = C\Delta T$$

• Specific heat capacity (C_s): Amount of heat required to raise the temperature of 1g of a substance by 1°C or 1K.

$$q = C_s \times m \times \Delta T$$

• Molar Heat Capacity (C_m): Amount of heat required to raise the temperature of 1 mole of a substance by 1°C or 1K.

$$q = C_m \times n \times \Delta T$$

- **Standard State of a Substance :** The standard state of a substance at a specified temperature is its, pure form at 1 bar.
- Standard Enthalpy of Formation ($\Delta_f H^\theta$): Enthalpy change accompanying the formation of one mole of a substance from its constituent elements under standard condition of temperature (normally 298 K) and pressure (1 bar).
 - ho $\Delta_f H^{\theta}$ of an element in standard state is taken as zero.
 - \triangleright Compounds with ve value of $\triangle_f H^{\theta}$ are more stable than their constituents.
 - $\Delta_r H^\circ = \Sigma_i a_i \Delta_f H^\theta$ (products) $-\Sigma_i b_i \Delta_f H^\theta$ (reactants): Where 'a' and 'b' are coefficients of products and reactants in balanced equation.
- Standard Enthalpy of Combustion ($\Delta_c \mathbf{H}^{\theta}$): Enthalpy change accompanying the complete combustion of one mole of a substance under standard conditions (298 K, 1 bar)
- Hess's Law of Constant Heat Summation: The total enthalpy change of a reaction remains same whether it takes place in one step or in several steps.
- **Bond Dissociation Enthalpy :** Enthalpy change when one mole of a gaseous covalent bond is broken to form products in gas phase. For example: $\text{Cl}_2(g) \to 2\text{Cl}(g)$; $\Delta_{\text{Cl-Cl}} H^\theta = 242\text{k/mol}^{-1}$.
- (i) For diatomic gaseous molecules; Bond enthalpy = Bond dissociation Enthalpy = Atomization Enthalpy.
- (ii) For Polyatomic gaseous molecules; Bond Enthalpy = Average of the bond dissociation enthalpies of the bonds of the same type.
- $\Delta_r H^{\theta} = \Sigma \Delta_{bond} H^{\theta}$ (Reactants) $\Sigma \Delta_{bond} H^{\theta}$ (Products).
- **Spontaneous Reaction :** A reaction which can take place either of its own or under some initiation.

- Entropy (S): It is measure of degree of randomness or disorder of a system. $\Delta S_{sys} = \frac{(q_{rev})_{sys}}{\Delta T} = \frac{(\Delta H)_{sys}}{\Delta T}$. Unit of Entropy = JK⁻¹ mol⁻¹
- **Second Law of Thermodynamics :** For all the spontaneous processes totally entropy change must be positive.

$$\Delta S_{\text{total}} = \Delta S_{svs} + \Delta S_{surr} > 0$$

• Gibbs Helmholtz Equation for determination of Spontaneity:

$$\Lambda G = \Lambda H - T\Lambda S$$

- (i) If $\Delta G = -ve$, the process is spontaneous
- (ii) If $\Delta G = +$ ve, the process is non-spontaneous
- (iii) If $\Delta G = 0$, the process is in equilibrium
- Relation between Gibbs Energy Change and Equilibrium Constant : $\Delta G^{\theta} = -2.303 \text{ RT log K}_c$.
- Third law of thermodynamic: The entropy of a perfectly crystalline solid at absolute zero (0 K) is taken to be zero.

1 - Mark Questions

- 1. Name the thermodynamic system to which following belong:
 - (i) Human body (ii) Milk in Thermos flask (iii) Tea in steel kettle
- **2.** Identity State functions out of the following : Enthalpy, Entropy, Heat, Temperature, Work, Free energy.
- **3.** Give two examples of state functions.
- 4. Write the mathematical statement of first law of thermodynamics.
- 5. Predict the internal energy change for an isolated system? [Ans. Zero]
- **6.** Why ΔH is more significant than ΔU ?
- **7.** Write one example each of extensive and intensive properties.
- **8.** Write a chemical equation in which ΔH and ΔU are equal.
- 9. Write the relationship between ΔH and ΔU for the reaction : $C(s) + O_2(g) \rightarrow CO_2(g)$.

- **10.** Define standard enthalpy of formation.
- 11. Why is the standard enthalpy of formation of diamond not zero although it is an element?
- 12. The enthalpy of atomization of CH_4 is 1665 kJ mol⁻¹. What is the bond enthalpy of C-H bond? [Ans. 416.25 kJ]
- 13. Identify the species for which $\Delta_f H^{\theta} = 0$, at 298 K : $-Br_2$, Cl_2 , CH_4 .

 [Hint: $Cl_2(Br_2 \text{ is liquid at 298K})$]
- **14.** For the reaction $2Cl(g) \rightarrow Cl_2(g)$; what are the sign of ΔH and ΔS ?
- **15.** For an isolated system $\Delta U = 0$, what will be ΔS ?
- **16.** Why entropy of steam is more than that of water at its boiling point?
- 17. Out of Diamond and Graphite which has higher entropy?
- **18.** Write an example of endothermic spontaneous reaction.
- 19. State second law of thermodynamics.
- **20.** State third law of thermodynamics.
- **21.** Which has more entropy ? 1 mol $H_2O(l)$ at 25°C or 1 mol $H_2O(l)$ at 35°C.
- 22. At what temperature the entropy of a perfectly crystalline solid is zero?
- **23.** For a certain reaction $\Delta G^{\theta} = 0$, what is the value of K_c ?
- 24. How can a non spontaneous reaction be made spontaneous?
- **25.** For a reaction both ΔH and ΔS are negative. Under what conditions does the reaction occur.

2 - Marks Question

1. In a process 701 J of heat is absorbed by a system and 394 J work is done by the system. What is the change in internal energy for the process?

- 2. Neither q nor w is state functions but q + w is a state function. Explain.
- **3.** Classify the following as extensive or intensive properties : Heat capacity, Density, Temperature, Molar heat capacity.
- **4.** Derive the relationship between ΔH and ΔU .
- 5. Derive the relationship $C_p C_v = R$.
- 6. A 1.25g sample of octane (C_8H_{18}) is burnt in excess of oxygen in a bomb calorimeter. The temperature of the calorimeter rises from 294.05 to 300.78K.If heat capacity of the calorimeter is 8.93 kJ K⁻¹. Find the heat transferred to calorimeter. [Ans. 0.075 kJ]
- 7. Show that for an ideal gas, the molar heat capacity under constant volume conditions is equal to 3/2 R.
- 8. Expansion of a gas in vacuum is called free expansion. Calculate the work done and change in internal energy when 1 mol of an ideal gas expands isothermally from I L to 5 L into vacuum.
- 9. State and explain Hess's Law of Constant Heat Summation with a suitable example.
- **10.** Derive the relationship between ΔH and ΔU . Given, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; $\Delta_r H^\circ = -92.4 \text{ kJ mol}^1$; What is the standard enthalpy of formation of NH_3 gas? [Ans. $-46.2 \text{ kJ mol}^{-1}$]
- 11. Calculate the enthalpy change for the reaction : $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$. Given the bond enthalpies H_2 , Br_2 and HBr are 435 kJ mol⁻¹, 192 kJ mol⁻¹ and 368 kJ mol⁻¹ respectively. [Ans. 109 kJ mol⁻¹]
- **12.** Is the bond dissociation enthalpy of all the four C-H bonds in CH₄ same? Give reason in support of your.
- **13.** Define the term entropy. Write its unit. How does entropy of a system change on increasing temperature?

- **14.** Dissolution of ammonium chloride in water is endothermic but still it dissolves in water readily. Why?
- **15.** Calculate the entropy change in the surroundings when 1.00 mol of $H_2O(I)$ is formed under standard conditions; $\Delta_f H^{\theta} = -286 \text{ kJ mol}^{-1}$.

 $[{f Ans.}~959.7~J~K^{-1}~mol^{-1}]$

- **16.** The enthalpy of vaporization of a liquid is 30 kJ mol⁻¹ and entropy of vaporization is 75 J K⁻¹ mol⁻¹. Calculate the boiling point of liquid at 1 atm. [Ans. 400 K]
- 17. The equilibrium constant for a reaction is 10. What will be the value of ΔG^{θ} ? R = 8.314J K⁻¹ mol⁻¹, T = 300 K. [Ans. 5.527 kJ mol⁻¹]
- **18.** Derive the relationship, $\Delta G = -T\Delta S_{total}$ for a system.
- 19. The ΔH and ΔS for $2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g)$ are given 61.17 kJ mol⁻¹ and 132 JK⁻¹ mol⁻¹ respectively. Above what temperature will the reaction be spontaneous? [Ans. > 463.4 K]

3 - Mark Questions

- 1. Differentiate between the following (with examples):
 - (i) Open and Closed System.
 - (ii) Adiabatic and Isothermal process
 - (iii) State function and path function
- Calculate the maximum work obtained when 0.75 mole of an ideal gas expands isothermally and reversibly at 27°C from a volume of 15 L to 25 L.
 [Ans. 955.7 J]
- 3. Calculate the number of kJ necessary to raise the temperature of 60 g of aluminium from 35 to 55°C. Molar heat capacity of Al is 24 J mol⁻¹J mol⁻¹K⁻¹. [Ans. 1.067kJ]

4. The reaction of cyanamide, NH₂CN(s), with Dioxygen was carried out in a bomb calorimeter, and ΔU was found to be – 742.7 kJ mol⁻¹ at 298K. Calculate Enthalpy change for the reaction at 298K,

$$NH_2CN(s) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(I)$$
[Ans. - 741.5 kJ mol⁻¹]

5. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are -890.3 kJ mol⁻¹, -393.5 kJ mol⁻¹ and -285.8 kJ mol⁻¹ respectively. Calculate enthalpy of formation of methane gas.

$$[Ans. - 74.8 \text{ kJ mol}^{-1}]$$

- **6.** Explain the Born Haber Cycle to determine the lattice enthalpy of NaCl.
- 7. Enthalpies of formation of CO(g), CO₂(g), N₂O(g) and N₂O₄(g) are -110, -393, 81 and 9.7 kJ mol⁻¹ respectively. Find the value of Δ_r H for the reaction; N₂O₄(g) + 3CO(g) \rightarrow N₂O(g) + 3CO₂(g).

$$[Ans. - 777.7 \text{ kJ mol}^{-1}]$$

8. The combustion of 1 mol of benzene takes place at 298K . After combustion CO_2 and H_2O are formed and 3267 kJ mol⁻¹ of heat is liberated. Calculate $\Delta_f H^{\theta}(C_6H_6)$.

Given :
$$\Delta_f H^{\theta}(CO_2) = -286 \text{ kJ mol}^{-1}$$
, $\Delta_f H^{\theta}(H_2O) = -393 \text{ kJ mol}^{-1}$ [Ans. 48.51 kJ mol $^{-1}$]

 Calculate the standard enthalpy of formation of CH₃OH (1) from the following data:

$$\begin{aligned} \text{CH}_3\text{OH} \ (1) + \frac{3}{2}\,\text{O}_2(g) \to \text{CO}_2(g) + 2\text{H}_2\text{O} \ (1); \ \Delta_c\text{H}^\theta = -726 \text{ kJ mol}^{-1} \\ \text{C}(g) + \text{O}_2(g) \to \text{CO}_2(g); \ \Delta_f\text{H}^\theta = -393 \text{ kJ mol}^{-1} \\ \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \to \text{H}_2\text{O}(1); \ \Delta_f\text{H}^\theta = -286 \text{ kJ mol}^{-1} \\ & [\textbf{Ans.} - 239 \text{ kJ mol}^{-1}] \end{aligned}$$

10. For oxidation of iron, 4 Fe(s) + $3O_2(g) \rightarrow 2\text{Fe}_2O_3(s)$ entropy change is $-549.4 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K. In spite of negative entropy change of this reaction, why is the reaction spontaneous ? ($\Delta_p H^\theta$ for this reason is $-1648 \text{ kJ mol}^{-1}$)

[Ans. $\Delta S_{\text{total}} = +4980.6 \text{ J K}^{-1} \text{ mol}^{-1}$]

11. Give reasons:

- (i) Evaporation of water is an endothermic process but it is spontaneous.
- (ii) A real crystal has more entropy than an ideal crystal.
- (iii) Entropy of universe is increasing.
- 12. For the reaction at 298 K, $2A + B \rightarrow C$; $\Delta H = 400 \text{ kJ mol}^{-1}$, $\Delta S = 0.2 \text{ kJ }$ $K^{-1} \text{ mol}^{-1}$. At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

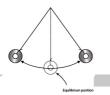
[Ans.
$$T > 2000 \text{ K}$$
]

- 13. Reaction X \rightarrow Y; $\Delta H = + ve$ is spontaneous at temperature "T". Determine
 - (i) Sign of ΔS for this reaction.
 - (ii) Sign of ΔG for $Y \rightarrow X$
 - (iii) Sign of ΔG at a temperature < T.

5 - Mark Questions

- 1. (a) What is reversible process in Thermodynamics?
 - (b) Name the thermodynamic processes for which : (i) q = 0 (ii) $\Delta U = 0$
 - (iii) $\Delta V = 0$ (iv) $\Delta P = 0$.
 - (c) Water decomposes by absorbing $286.2 \, \text{kJ}$ of electrical energy per mole. When H_2 and O_2 combine to form one mole of H_2O , $286.2 \, \text{kJ}$ of heat is produced. Which thermodynamic law is proved? Write its statement.
- 2. (a) Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain. [Hint: $q_v = \Delta U$ and $q_p = \Delta H$]
 - (b) It has been found that 221.4 J is needed to heat 30g of ethanol from 15°C to 18°C. Calculate (a) specific heat capacity, and (b) molar heat capacity of ethanol. [Ans. (a) 2.46 Jg⁻¹°C⁻¹, (b) 113.2 J mol⁻¹C⁻¹]

- 3. (a) Differentiate the terms Bond dissociation enthalpy and Bond Enthalpy.
 - (b) Calculate enthalpy change for the process $CCl_4(g) \rightarrow C(g) + 4Cl(g)$ and calculate Bond enthalpy of C-C1 bond in CCl_4 . Given: $\Delta_{vap} H^{\theta}(CCl_4) = 30.5 \text{ kJ mol}^{-1}$; $\Delta_f H^{\theta}(CCl_4) = -135.5 \text{ kJ mol}^{-1}$; $\Delta_a H^{\theta}(C) = 715 \text{ kJ mol}^{-1}$ and $\Delta_a H^{\theta}(Cl_2) = 242 \text{ kJ mol}^{-1}$ [Ans. 1304 kJ mol⁻¹, 326 kJ mol⁻¹]
- **4.** Predict the sign of ΔS for the following changes :
 - (i) Freezing of water,
 - (ii) $C(graphite) \rightarrow C(diamond)$
 - (iii) $H_2(g)$ at 298 k and 1 bar $\rightarrow H_2(g)$ at 298 k and 10 bar
 - (iv) $H_2(g) + I_2(g) \to 2HI(g)$
 - (v) $2\text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)$
- **5.** (i) Define Gibbs free energy. Give its mathematical expression. What is Gibb's energy criteria of spontaneity.
 - (ii) For the reaction : $2A(g) + B(g) \rightarrow 2D(g)$, $\Delta U^{\theta} = -10.5$ kJ and $\Delta S^{\theta} = -44.1$ J K⁻¹. Calculate $\Delta_r G^{\theta}$ for the reaction, and predict whether will occur spontaneously. [Ans. $\Delta_r G^{\theta} = +0.16$ kJ, Non spontaneous]



Chapter - 7

Equilibrium

- Equilibrium: It is a state in a process when two opposing processes (forward and reverse) occur simultaneously at the same rate. The free energy change at equilibrium state is zero *i.e.*, $\Delta G = 0$.
- Equilibrium constant: For a general reaction:

$$aA + bB \iff cC + dD$$

$$\mathbf{K}_c = \frac{[\mathbf{C}]^c [\mathbf{D}]^d}{[\mathbf{A}]^a [\mathbf{B}]^b} \text{ and } \mathbf{K}_p = \frac{\mathbf{P}_{\mathbf{C}}^c \times \mathbf{P}_{\mathbf{D}}^d}{\mathbf{P}_{\mathbf{A}}^a \times \mathbf{P}_{\mathbf{B}}^b}$$

• Relationship between K_p and K_c :

$$\begin{split} \mathbf{K}_p &= \mathbf{K}_c \, (\mathrm{RT})^{\Delta n} \mathbf{g} \\ \Delta n_g &= n_p(g) - n_r(g) \end{split}$$

• Magnitude of equilibrium constant depends upon the way in which a reaction is written:

Chemical equation	Equilibrium constant
aA + bB	K
cC + dD = aA + bB	$K_1 = \frac{1}{K}$
$naA + nbB \Longrightarrow ncC + ndD$	$K_2 = K^n$
$\frac{1}{n}aA + \frac{1}{n}bB \Longrightarrow \frac{1}{n}cC + \frac{1}{n}dD$	$K_3 = K^{1/n}$

Predicting the direction of reaction :

If $Q_c = K_c \Rightarrow$ the reaction is in a state of equilibrium.

 $Q_c > K_c \Rightarrow$ the reaction proceeds in reverse direction.

 $Q_c < K_c \Rightarrow$ the reaction proceeds in forward direction.

- Ostwald's dilution law : Degree of dissociation of weak electrolyte, $\alpha = \sqrt{\frac{K}{C}}$
- Ionic Product of water $(K_w) = [H_3O^+] [OH^-] = 10^{-14}$ at 298K
- Le-Chatelier's Principle: When a system of equilibrium is subjected to a change in temperature, pressure or concentration, the equilibrium shifts itself in such a way so as to undo or nullify the effect of change.
- Outcomes of Le-Chatelier's Principle

Change at equilibriumShift in equilibriumIncrease in temperatureEndothermic directionDecrease in temperatureExothermic directionIncrease in pressureTowards lesser gaseous molesDecrease in pressureTowards greater gaseous molesIncrease in Conc. of reactantsForward directionIncrease in Conc. of productsReverse direction

• Conjugate Acid or Base : Acid-base pair which differ by H⁺ ion.

Species $-H^+$ = Conjugate base Species $+H^+$ = Conjugate acid

pH of solution :

$$pH = -log~[H_3O^+]~or~[H^+] = 10^{-pH}~,~pOH = -log~[OH^-] \\ pH + pOH = pK_w = 14~at~298K$$

- Common ion effect: The depression of ionisation of weak electrolyte by the presence of common ion from a strong electrolyte is called common ion effect. For example degree of dissociation of NH₄OH decreases in the presence of strong electrolyte NH₄Cl.
- Hydrolysis of salts and pH of their solutions: Hydrolysis of salt is defined as the reaction of cation or anion with water as a result of which the pH of water changes.
 - 1. Salts of strong and strong bases (e.g., NaCl) do not hydrolyse. The solution pH will be 7.
 - 2. Salts of weak acids and strong bases (e.g., CH_3COONa) hydrolyse, pH >7 (The anion acts as a base).

$$X^- + H_2O \Longrightarrow HX + OH^-$$
(Weak acid) (Weak base)

$$pH = 7 + \frac{1}{2} (pK_a + \log C)$$

3. Salt of strong acids and weak bases (*e.g.*, NH₄Cl) hydrolyse, pH < 7. (The cation acts as an acid).

$$M^+ + H_2O \longrightarrow MOH + H^+$$

 $pH = 7 - \frac{1}{2} (pK_b + logC)$

4. Salt of weak acids and weak base (e.g., CH_3COONH_4) hydrolyse. The cation acts as an acid and anion as a base but whether the solution is acidic or basic depends upon the relative values of K_a and K_b for these **ions.**

$$M^+ + X^- + H_2O \Longrightarrow MOH + HX$$

 $pH = 7 + \frac{1}{2} (pK_a - pK_b)$

- **Buffer solutions :** The solutions, which resist the change in pH on dilution or addition of small amounts of acid or base, are called buffer solutions.
- Basic buffer: Solution of weak base and its salt with strong acid, For e.g., NH₄OH + NH₄Cl
- **Acidic buffer :** Solution of weak acid and its salt with strong base, For *e.g.*, CH₃COOH + CH₃COONa.
- Henderson Hasselbalch Equation for the pH of Buffer solution—

$$pH = pK_a + log \frac{[Salt]}{[Acid]}$$
 (for acidic buffer)

$$pOH = pK_a + log \frac{[Salt]}{[Base]}$$
 (for basic buffer)

• Solubility Product (K_{sp}) : The equilibrium constant that represent the equilibrium between undissolved salt (solute) and its ions in a saturated solution is called solubility product constant (K_{sp}) .

For
$$A_x B_y \stackrel{aq}{=} x A^{y+} + y B^{x-}$$

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y = (xs)^x (ys)^y = x^x. \ y^x. \ s^{(x+y)}$$
where $s = \text{Molar solubility}$

If ionic product $\leq K_{sp}$; salt remain dissolve.

If ionic product $> K_{sp}$; salt will be precipitated.

Relationship between solubility (s) and solubility product (K_{sp}) .

$$\mathbf{K}_{SD} = \mathbf{x}^{x}.\mathbf{y}^{y}. \mathbf{s}^{x+y}$$

For binary salts (e.g., AgCl, AgBr, AgI)

$$K_{sp} = s^2$$

For Ternary salts (e.g., PbI₂)

$$K_{sp} = s^2$$
$$K_{sp} = 4s^3$$

1 - Mark Questions

- 1. Define physical equilibrium. Give an example also.
- 2. Fizz is observed when soda water bottle is opened. Why?
- 3. Justify the statement: 'Both physical and chemical equilibria are dynamic in nature'
- 4. State Henry's law.
- 5. In a reversible reaction, the two substances are in equilibrium. If the concentration of each one is reduced to half, then what is the effect on the equilibrium constant?
- **6.** K_1 and K_2 are equilibrium constant for reactions (1) and (2)
 - (1) $N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$
 - (2) $NO(g) \rightleftharpoons 1/2 N_2(g) + 1/2 O_2(g)$

calculate the relation between K₁ and K₂

7. Write the equilibrium constant expression for the following reaction:

$$3 \operatorname{Fe}(s) + 4 \operatorname{H}_2 O(g) \rightleftharpoons \operatorname{Fe}_3 O_4(s) + 4 \operatorname{H}_2(g)$$

8. Classify the equilibrium as homogenous or heterogenous :

$$\mathrm{CH_{3}COOC_{2}H_{5}(aq)} + \mathrm{H_{2}O(1)} \rightleftharpoons \mathrm{CH_{3}COOH(aq)} + \mathrm{C_{2}H_{5}OH} \ (aq)$$

9.
$$K_p = \frac{(P_{NH_3})}{(P_{H_2})^{3/2}(P_{N_2})^{1/2}}$$

Write the balanced chemical equation corresponding to the above expression.

- 10. Give the direction in which the reaction would proceed if $Q_c > K_c$.
- 11. $Hb(s) + O_2(g) \rightleftharpoons HbO_2(s)$

Predict the direction in which equilibrium gets shifted if partial pressure of $O_2(g)$ is lowered.

12. Discuss the position of equilibrium if the following reaction is carried out in the presence of catalyst.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

13. In which case the yield of the product will be more.

$$A \rightleftharpoons B$$
 $K_1 = 10^{10}$
 $X \rightleftharpoons Y$ $K_2 = 10^6$

- **14.** Value of K_c at 500 K for $A + 2B \rightleftharpoons C$ is 10.6

 Determine the value of K_c at the same temperature for $C \rightleftharpoons A + 2B$
- 15. Why do we sweat more on a humid day?
- 16. Why does a catalyst not affect the magnitude of equilibrium constant?
- 17. Write the relation between K_p and K_c for the given reaction. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
- **18.** Write the expression of Kc for the following reaction $CH_3COOC_2H_5(l) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$
- 19. Write the expression of Kp for the following reaction

$$Cu(NO_3)_2(s) \rightleftharpoons 2 CuO(s) + 4NO_2(g) + O_2(g)$$

- **20.** For an exothermic reaction, what happens to the equilibrium constant if temperature is increase?
- **21.** K_a for HA₁ is 10 and K_a for HA₂ is 12 Which acid is stronger.
- 22. For tribasic acid Ka₁ > Ka₂ > Ka₃What will happen to the acid strength of polyprotic acid if protons are lost?
- 23. C(s) Diamond (Density = 3.5 g/cm³) ⇒ C(s) Graphite (Density = 2.3 g/cm³)

What will be the effect of increasing the pressure in this equilibrium.

- **24.** Under what condition does the active mass becomes equal to the molarity?
- **25.** Which expression of K_c or K_{eq} , involved solutions and gases only?
- **26.** What will be the change in the direction of equilibrium if Ne gas is added in a reaction at constant volume?
- **27.** What will be the effect on the boiling point of liquid if pressure is increased?

2 - Mark Questions

1. What is Kc for the following equilibrium when the equilibrium concentration of each substance is:

$$[SO_2] = 0.60M$$
, $[O_2] = 0.82$ M and $[SO_3] = 1.90$ M?
 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

2. At a certain temperature and total pressure of 10⁵ Pa, iodine vapour contains 40% by volume of I atoms

$$I_2(g) \rightleftharpoons 2I(g)$$

Calculate Kp for the equilibrium.

[Ans. $2.67 \times 104 \text{ Pa}$]

- **3.** Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?
- **4.** A sample of HI(g) is placed in flask at a pressure of 0.2 atm. At equilibrium the partial pressure of HI(g) is 0.04 atm.

What is Kp for the given equilibrium?

$$2 \operatorname{HI}(g) \longrightarrow \operatorname{H}_{2}(g) + \operatorname{I}_{2}(g)$$
 [Ans. 4]

5. One mole of H₂O and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation,

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Calculate the equilibrium constant for the reaction.

[Ans. 0.444]

6. At 1127 K and 1 atm pressure, a gaseous mixture of CO and $\rm CO_2$ in equilibrium with soild carbon has 90.55% CO by mass

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

Calculate Kc for this reaction at the above temperature. [Ans. 0.153]

- 7. Describe the effect of:
 - (a) addition of H₂
 - (b) addition of CH₃OH
 - (c) removal of CO
 - (d) removal of CH₃OH

on the equilibrium of the reaction:

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$

8. $A + 3 B \rightleftharpoons 2X ; K = x$

What will be the equilibrium constant for the decomposition of 1 mol of x?

9. $N_2(g) + 3H_2(g) \rightleftharpoons 2 NH_3(g)$; — K_1

$$N_2(g) + O_2(g) \rightleftharpoons 2 \text{ NO}(g)$$
 ; — K_2

$$H_2(g) + 1/2O_2(g) \rightleftharpoons H_2O(g)$$
; — K_3

Determine the equilibrium constant for

$$2 \text{ NH}_3(g) + 5/2O_2(g) \rightleftharpoons 2NO(g) + 3H_2O)(g).$$

10. K_c for $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl(g)$ is 0.04 at 25°C

How much mole of PCl₅ must be added to 3 L flask to obtain a chlorine concentration of 0.15 M? [Ans. 2.1]

3 - Mark Questions

- 1. Four moles of PCl₅ are heated in a closed 4 dm³ container to reach equilibrium at 400 K. At equilibrium 50% of PCl₅ is dissociated. What is the value of K_c for the dissociation of PCl₅ into PCl₃ and Cl₂ at 400 K

 [Ans. 0.50]
- **2.** (a) How does the value of equilibrium constant predict the extent of a reaction?
 - (b) Equilibrium constant for a reaction is 10. What will be the equilibrium constant for the reverse reaction?
- **3.** (a) Define the equilibrium constant.
 - (b) For the general reaction:

$$a A(g) + b B(g) \rightleftharpoons c C(g) + d D(g).$$

Derive the relationship between Kp and Kc

- **4.** (a) What is meant by dynamic nature of equilibrium?
 - (b) Consider the following transformation.

$$A \rightleftharpoons B$$

$$K_1 = 1$$

$$B \rightleftharpoons C$$

$$K_2 = 2$$

$$C \rightleftharpoons D$$

$$K_3 = 3$$

Calculate the value of K for $A \rightleftharpoons D$

5. K_c for $SO_2(g) + 1/2 O_2(g) \rightleftharpoons SO_3(g)$ at 600°C is 61.7

Calculate K_p . What is the unit K_p for the above equilibrium. [R = 0.0821 L atm K^{-1} mol⁻¹]

6. 3.2 mole of HI were heated in a sealed bulb at 444°C till the equilibrium state was reached. Its degree of dissociation was found to be 20%. Calculate the number of moles hydrogen iodide, hydrogen and iodine present at the equilibrium point and also determine the equilibrium constant.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
.

- 7. At 25°C and 1 atm, the partial pressure in an equilibrium mixture of N_2O_4 NO_2 are 0.7 and 0.3 atm, respectively. Calculate the partial pressure when they are in equilibriums at 25°C and at a total pressure of 10 atm.
- **8.** 13.8 g of N_2O_4 was placed in a 1L reaction vessel at 400 K and allowed to attain equilibrium: N_2O_4 (g) $\rightleftharpoons 2NO_2$ (g)

The total pressure at equilbrium was found to be 9.15 bar. Calculate K_c , K_p and partial pressure at equilibrium. $[K_c = 2.6]$

9. The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K

$$H_2(g) + Br(g) \rightleftharpoons 2HBr(g)$$

Find the equilibrium pressure of all gases if 10.0 bar a HBr is introduced into a sealed container at 1024 K.

$$[P_{H_2} eq. = P_{Br_2} eq. = 2.5 \times 10^{-2} \text{ bar}; P_{HBr} = 10.0 \text{ bar}]$$

- **10.** In a reaction: $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(l) \Delta_r H^{\theta} = -92 \text{ kJ/mol}$ Indicate the direction in which equilibrium will shift when:-
 - (i) Temperature is decreased.
 - (ii) Pressure is decreased.
 - (iii) Ne gas is added at constant pressure.

5 - Mark Questions

1. Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

- (a) Write as expression for Kp for the above reaction.
- (b) How will the values of Kp and composition of equilibrium mixture be affected by:
 - (i) increasing the pressure
 - (ii) increasing the temperature
 - (iii) using a catalyst?

2. At 473 K, equilibrium constant Kc for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3} . If decomposition is depicted as,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \Delta H^{\theta} = 124.0 \text{ kJ mol}^{-1}$$

- (a) Write an expression for Kc for the reaction.
- (b) What is the value of Kc for the reverse reaction at the same temperature?
- (c) What would be the effect on Kc if (i) PCl_5 is added (ii) pressure is increased (iii) the temperature is increased? [(b) $K_C = 120.48$ (c)
- (i) No effect (ii) No effect (iii) Kc increase]
- **3.** Ammonia is prepared by Haber's process is which the following reaction occurs

$$N_2(g) + 3H_2(g) \rightleftharpoons 2 NH_3(g) \Delta H^{\theta} = -93.6 \text{ kJ}$$

Mention the effect of following on the equilibrium concentration of ammonia:-

- (a) Increasing pressure
- (b) Increasing temperature
- (c) Use of catalyst at an optimum temperature.
- (d) Addition of inert gas at constant volume.
- (e) Addition of inert gas at constant pressure.
- **4.** Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as :

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

- (i) Write the concentration ratio (reaction quotient), Qc, for this reaction (note: water is not in excess and is not a solvent in this reaction)
- (ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.
- (iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached?
 - [(ii) 3.92 (iii) Qc = 0.204, Equilibrium has not been attained.]

Ionic Equilibrium

1 - Mark Questions

- 1. Which of the following are Lewis acids? H₂O, BF₃, H⁺, NH₄⁺
- 2. Write the conjugate acids for the following Bronsted bases. C₆H₅OH, H₂O
- Write the conjugate bases for the following Bronsted acids.
 H₂O, CH₃COOH.
- 4. Which of the following are Lewis acids?(a) H₂O, (b) AlCl₃ (c) NH₄⁺
- 5. Define the Ostwald's dilution law.
- **6.** SO₃²⁻ is Bronsted base or acid and why?
- 7. Why pH of our blood remains almost constant at 7.4 though we quite often eat spicy food?
- 8. pH of black coffee is 5.0 at 25°C. Is black coffee acidic or basic?

 [Ans. Acidic]
- **9.** What will be the value of (pKa + pKb) at 25°C.
- 10. What will be the pH of 1 M KNO₃ solutions at 25°C?
- **12.** Why does the solubility of CO₂ decrease with rise in temperature?
- 13. The solubility of $A_2 X_3$ is y mol dm⁻³. Calculate its solubility product.
- **14.** Write the Ksp expression for Al (OH)₃
- **15.** What is the condition for precipitation of a salt?
- **16.** Pridict whether the solution is acidic, basic or natural when NH₄NO₃ undergo hydrolysis.
- 17. Explain why pure NaCl precipitates out when HCl gas is passed through the solution of NaCl?
- 18. Give the Henderson's -Hasselbalch equation for an acidic buffer solution.
- **19.** On which of the factors the equilibrium depend: Temperature, nature of reactant and product, initial concentration and pressure of the reactants.

- **20.** What are amphoteric substances? Give one example.
- **21.** What could be the temperature 15°C or 100°C for $Kw = 7.5 \times 10^{-14}$?
- **22.** What happens to ionic product of water if some acid is added to it?
- **23.** What is the conjugate base of HCO_3^- ?

- 1. Explain ionic product of water. What is the effect of temperature on ionic product of water?
- 2. What is pOH? What is its value for neutral water at 25°C?
- 3. (a) Define buffer solution.
 - (b) Give one example each of acidic and basic buffer.
- **4.** The solubility of $Ca_3(PO_4)_2$ in water is x moles / litre. Calculate its solubility product. [Ans. $108x^5$]
- 5. Calculate the pH of a 0.01 M solution of acetic acid. K_a for CH₃COOH is 1.8×10^{-5} at 25°C. [Ans. 3.37]
- **6.** Calculate pH when $9.8 \text{ g H}_2\text{SO}_4$ is dissolved in 2 litre of solution. [1]
- 7. Calculate the pH of 10^{-9} M HCl. [Ans. pH = 6.9957]
- 8. An acid having pH = 6 is diluted 100 times. What will be the pH of the final solution?

 [Ans. pH = 6.98]
- 9. Calculate the pH of 10^{-10} M NaOH solution. [Ans. pH = 7.0004]
- 10. Solid Ba(NO₃)₂ is gradually dissolved in a 1.0×10^{-4} M Na₂CO₃ solution. At what concentration of Ba²⁺ will a precipitation took place? (K_{sp} for BaCO₃ = 5.1×10^{-9}) [Ans. 5.1×10^{-5} M]
- **11.** The pKa of acetic acid and pKb of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.

[Ans. 7.005]

3-Mark Questions

- 1. What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:
 - HNO₂, CN⁻, HClO₄, F⁻, OH⁻, OH₃⁻, and S²⁻.
- 2. Define solubility product. Calculate the solubility product of $Ca(OH)_2$ if its solubility is 3 moles L^{-1} . [Ans. $K_{sp} = 108$]

- Calculate the pH of the following mixture.
 200 mL of M/10 H₂SO₄ + 400 mL of M/10 H₃PO₄ + 400 mL of M/10 HCl. [0.69]
- **4.** The solubility product of AgCl in water is 1.5×10^{-10} . Calculate its solubility in 0.01 M NaCl aqueous solution. [1.5 × 10–8 M]
- 5. Predict whether a precipitate will be formed or not on mixing 20 ml of 0.001 M NaCl solution with 80 mL of 0.01 M AgNO₃ solution, Ksp for AgCl is 1.5×10^{-10} . [Yes, ppt. will be formed]
- **6.** Equal volumes of three acids solution with pH 3, 4 and 5 are mixed in a vessel. What will be the H⁺ ion concentration in the mixture?
- 7. Calculate the pH of a solution obtained by mixing 50 mL of 0.2 M HCl and 50 mL of 0.1 M NaOH. [Ans. 1.3010]
- 8. The pH of 0.1 M hydrocyanic acid solution is 5.2. What is the value of K_a for hydrocyanic acid? [Ans. $Ka = 3.69 \times 10^{-10}$]
- 9. A buffer solution is prepared by mixing equal concentration of weak base and its salt with strong acid. For the base K_b is given as 10^{-9} . Calculate the pH of the buffer solution. [5]
- 10. Calculate the pH of the resultant mixtures:
 - (a) 10 mL of 0.2 M Ca(OH)₂ + 25 mL of 0.1 M HCl
 - (b) 10 mL of 0.01 M $H_2SO_4 + 10$ mL of 0.01 M $Ca(OH)_2$
 - (c) 10mL of 0.1 M H₂SO₄ + 10mL of 0.1 M KOH.

[(a) 12.632 (b) 7 (c) 1.3]

- 11. Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$). [NO ppt. will ocurr]
- 12. What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, $K_{sp} = 6.3 \times 10^{-18}$) [5.02 × 10⁻⁹ mol L⁻¹]
- 13. The ionization constant of aniline is 3.69×10^{-10} :
 - (i) Calculate pH of 0.01 M solution of aniline.
 - (ii) Calculate the degree of dissociation of aniline in the solution.
 - (iii) Calculate the ionization constant of conjugate acid of the aniline.

- **14.** The K_{sp} for Al(OH)₃ is 2.7×10^{-11} . Calculate its solubility in g/L and pH of this solution.
- 15. Calculate the volume of water required to dissolve 0.3 gm of $Zn(OH)_2$ to get a saturated solution. $K_{sp}[Zn(OH)_2] = 1 \times 10^{-15}$

[Given Atomic mass of Zn = 65.3, O = 16, H = 1 g mol⁻¹ respectively]

- **16.** The pH of an aqueous solution of ammonia is 11.5. Find the molarity of the solution. K_b (NH₄OH) = 1.8×10^{-5} [0.57]
- 17. What is the pH of the solution when 0.2 mole of HCl is added to 1 L of the solution containing 0.1 M each of CH₃COOH & acetate ion. Assume that volume is 1 L.

$$K_{a(CH_3COOH)} = 1.8 \times 10^{-5}.$$
 [1]

5 - Mark Questions

- 1. Calculate the pH value of the following solutions.
 - (a) 10^{-2} M HCl.
 - (b) $10^{-3} \text{ M H}_2\text{SO}_4$.
 - (c) 10⁻⁴ M NaOH
 - (d) 0.04 M NaOH.
 - (e) 0.03 M HCl. [Ans. (a) 2 (b) 2.6990 (c) 10 (d) 12.60 (e) 1.5229]
- 2. (i) Calculate the pH of a buffer solution containing 2.0 mol/L CH₃COOH in 1.0 mol/L of CH₃COONa . [Given K_a for CH₃COOH is 1.8×10^{-5} at 25°C.]
 - (ii) Calculate the change in pH of the buffer after the addition of 0.01 mol NaOH.
 - (iii) Calculate the pH of the buffer after the addition of 0.01 M HCl?

[**Ans.** (i) 4.4337, (ii) 0.0065, (iii) 4,4372]

- **3.** (a) What is solubility product? How is it different from ionic product?
 - (b) Calculate the solubility of PbCl₂ if its solubility product is 1.0×10^{-6} at 298 K. [Ans. 6.3×10^{-3} M]
- **4.** (a) Write short notes on the following:
 - (i) Common ion effect
 - (ii) Buffer solution

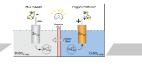
- (b) Calculate the pH of a buffer solution containing 0.2 mole of NH₄Cl and 0.1 mole of NH₄OH per litre. K_b for NH₄OH = 1.8×10^{-5} [Ans. 8.966]
- 5. 500 mL saturated solution of Ca(OH)₂ is mixed with equal volume of 0.4 M NaOH. How much Ca(OH)₂ in mg is precipitated?

$$[K_a (Ca(OH)_2) = 4.42 \times 10^{-5} \text{ at } 25^{\circ}C]$$

6. Calculate the pH of 0.1 M ammonia solution. Calculate the pH after 50 mL of this solution is treated with 25 mL of 0.1 M HCl.

(Given
$$K_b$$
 (NH₃) = 1.77 × 10⁻⁵.]





Chapter - 8

Redox **Reactions**

Oxidation and Reduction:

	Oxidation		Reduction
1.	Addition of oxygen	1.	Removal of oxygen
2.	Removal an Hydrogen	2.	Addition of Hydrogen
3.	Addition of an electronegative element.	3.	Removal of an electronegative element.
4.	Removal of an electropositive element	4.	Addition of an electropositive element.
5.	Loss of electron(s)	5.	Gain of electron(s)
6.	Increase in oxidation number.	6.	Decrease in oxidation number.

- Reducing Agent: Donor of electrons.
- Oxidising Agent : Acceptor of electrons.
- **Redox Reaction :** Reactions in which oxidation and reduction takes place simultaneously.
- Oxidation Number: It is charge that an atom appears to have in a given species when the bonding electron are counted towards more electronegative atom.

• Calculation of Oxidation Number :

- (a) Oxidation number of all the elements in their elemental form (in standard state) is taken as zero. Oxidation number of element in a molecule Cl_2 , F_2 , O_2 , P_4 , O_3 , Fe, H_2 , N_2 , C (graphite) is zero.
- (b) Common Oxidation number of elements of first group is +1. Common Oxidation number of elements of second group + 2.
- (c) For ions composed of only one atom, the oxidation number is equal to the charge on the ion.

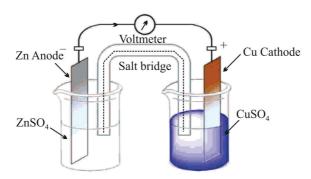
- (d) The oxidation number of oxygen in most compounds is -2. While in peroxides (e.g., H_2O_2 , Na_2O_2), each oxygen atom is assigned an oxidation number of -1, in super oxides (e.g., KO_2 , RbO_2) each oxygen atom is assigned an oxidation number of $-(\frac{1}{2})$.
- (e) In oxygen difluoride (OF_2) and dioxygen difluoride (O_2F_2), the oxygen is assigned an oxidation number of +2 and +1, respectively.
- (f) The oxidation number of hydrogen is + 1 but in metal hydride its oxidation no. is 1.
- (g) In all its compounds, fluorine has an oxidation number of -1.
- (h) The algebraic sum of the oxidation number of all the atoms in a compound must be zero.
- (i) In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion.
- Types of Redox Reactions:
 - (i) Combination Reaction : 0 0 +2 -3 $3 \text{ Mg (s)} + \text{N}_2 \text{ (g)} \xrightarrow{\Delta} \text{Mg}_3 \text{N}_2 \text{ (s)}$
 - (ii) Decomposition Reaction : +1+5-2 +1-1 0 $2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$
 - (iii) Metal Displacement : + 2 + 6 2 0 + 2 + 6 2 0 $CuSO_4$ (aq) + $Zn(s) \rightarrow ZnSO_4$ (aq) + Cu(s)
 - (iv) Non-metal displacement : 0 + 1 2 + 2 2 + 1 = 0 $Ca (s) + 2 H_2O (1) \rightarrow Ca (OH)_2 + H_2 (g)$
 - (v) Disproportionation reactions: It is a reaction in which same element is reduced and oxidized simultaneously.

0 -1 +1
C1₂ (g) +2 OH⁻ (aq)
$$\rightarrow$$
 Cl⁻ (aq) + ClO⁻ (aq) + H₂O (1)

- **Stock Notation**: Representing oxidation number of metal in Roman numerals within parenthesis after the symbol or name of metal in the molecular formula or name of a compound. For *e.g.*, Stock Notation of Ferric oxide is Fe₂(III)O₃ or Iron (III) oxide.
- Fractional Oxidation Number: When two or more atoms of an element are present in different oxidation states, then calculated oxidation number may comes out as fractional due to average of all the different oxidation states.

In reality no element can have a fractional oxidation state.

- Balancing of Redox Reactions:
 - (A) Oxidation number method
 - (B) Half reaction method
- Electrode Potential (E): Potential difference between electrode and electrolytic solution due to charge separation.
- Standard Electrode Potential (E^θ): Electrode Potential measured at 298 K and 1M concentration of metal ions (or 1 bar pressure of gas).
- **Electrochemical Cell:** A device in which chemical energy of a spontaneous redox reaction is converted into electrical energy.



Cell diagram: Zn | Zn²⁺ || Cu²⁺ | cu

LHS oxidation,

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$

RHS reduction

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

Overall reaction
$$\operatorname{Zn}(s) + \operatorname{Cu}^{2+}(aq) \to \operatorname{Zn}^{2+}(aq) + \operatorname{Cu}(s)$$

• Representation of an Electrochemical cell:

Flow of electrons
$$\longrightarrow$$
Flow of current \longrightarrow

$$Zn(s) | Zn^{2+}(aq) || Cu^{2+}(aq) | Cu(s)$$

LOAN	Left Electrode Oxidation	Salt Bridge	Right Electrode Reduction
	Anode		Cathode
	Negative		Positive

• Functions of Salt Bridge: (i) To complete inner circuit. (ii) To maintain electrical neutrality around electrudes.

Valency: Valency is the combining capacity of en element. Valency of an element cannot be zero.

Limitation of Concept of Oxidation Number

Acc. to the concept of oxidation number, oxidation means increase oxidation number, during, oxidation there is decrese in electron density while increase in electron density around the atom under going reduction.

1 - Mark Questions

- 1. Define oxidation and reduction according to electronic concept.
- 2. Define oxidation and reduction according to oxidation number.
- **3.** A freshly cut apple is almost white but it turns reddish brown after sometime. Give reason.
- 4. Define oxidation number.
- 5. Write oxidation number of Mn in KMnO₄.
- **6.** Write oxidation number of Cr in $Cr_2O_7^{2-}$.
- 7. Write Stock notation of MnO₂ and AuCl₃.
- **8.** Define redox reaction with example.
- **9.** Define disproportionation reaction. Give one example.
- 10. Define the term redox tirration.
- 11. Name the indicator used in redox titrations involving K₂Cr₂O₇ as an oxidizing agent.
- **12.** At what concentration of Cu²⁺ (aq) will electrode potential become equal to its standard electrode potential? [Ans. 1 M]
- 13. The standard reduction potentials of three metals cations X, Y and Z are + 0.52, -3.03 and -1.18 V respectively. Arrange X, Y and Z in order of increasing reducing power. [Ans. X < Z < Y]</p>
- **14.** An electrochemcial cell consists of two electrodes *i.e.*, Anode and Cathode. What is the direction of flow of electrons in this cell?
- 15. Why anode is negatively charged in an electrochemical cell.
- **16.** Out of Zn and Cu vessel one will be more suitable to store 1 M HCl?

[Ans. Cu]

Given
$$E_{Zn^{2+}/Zn}^{\theta} = -0.76 \text{ V}, E_{Cu^{2+}/Cu}^{\theta} = +0.34 \text{ V}.$$

15. Is it safe to stir 1 M AgNO₃ solution with copper spoon?

Given
$$E_{Ag^+/Ag}^{\theta} = +0.80 \text{ V}$$
, $E_{Cu^{2+}/Cu}^{\theta} = +0.34 \text{ V}$. [Ans. No]

2 - Mark Questions

1. Identify oxidant and reductant in the reaction:

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq).$$

- 2. Calculate oxidation number of Fe in Fe₃O₄ and write a suitable justification of your answer.
- 3. Oxidation-reduction reactions are complementary. Explain.
- **4.** Write formula for the following compounds :
 - (i) Mercury (II) chloride
 - (ii) Nickel (II) sulphate
 - (iii) Iron (III) sulphate
 - (iv) Chromium (III) oxide
- 5. Justify that the reaction : $H_2O(s) + F_2 \rightarrow HF + HOF$ is a redox reaction.
- **6.** A decomposition reaction may or may not be a redox reaction. Write two decomposition reactions in support of the statement.
- 7. Split the reaction $2 \text{ K (s)} + \text{C1}_2(\text{g}) \rightarrow 2 \text{ KC1 (s)}$ into oxidation and reduction half reactions.
- **8.** Calculate the oxidation number of underlined elements in following compounds:
 - $\text{(i) Ca}\underline{O}_2 \quad \text{(ii) } H_2\underline{S}_2O_7 \quad \text{(iii) } K_2\underline{Mn}O_4 \quad \text{(iv) } K\underline{I}_3$
- 9. Write the functions of salt bridge in an electrochemical cell.
- **10.** Define the term redox couple. Write the practical application of redox couple.
- 11. The standard reduction potentials of two metals A and B are 0.76 V and + 0.34 V respectively. An electrochemical cell is formed using electrodes of these metals.
 - (i) Identify the cathode and anode.
 - (ii) Write the direction of flow of electron.

- 1. Calculate oxidation number of:
 - (i) $\operatorname{Cr} \operatorname{in} \underline{\operatorname{Cr}_2} \operatorname{O_4}^{2-}$
 - (ii) O in KO_2
 - (iii) Na in Na₂O₂.
- 2. Account for the following:
 - (i) HNO₃ acts as oxidizing agent while HNO₂ can act both as reducing and oxidizing agent.
 - (ii) AgF₂ is unstable compound and act as a strong oxidizing agent.
 - (iii) Ozone acts as an oxidising agent.
- **3.** Permanganate ion (MnO₄⁻) reacts with sulphur dioxide gas in acidic medium to produce Mn²⁺ ion and hydrogen sulphate ion. Write ionic equation and balance by ion electron method.
- 4. Balance the following equation by oxidation number method:

$$P_4(s) + OH^-(aq) \rightarrow PH_3 + H_2PO_2^-(aq)$$
 [Basic Medium]

5. Balance the following equation in basic medium :

$$C1_{2}O_{7}(g) + H_{2}O_{2}(1) \rightarrow ClO_{2}^{-}(aq) + O_{2}(g)$$

6. Depict the galvanic cell in which the reaction

$$Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$
 takes place. Further show:

- (i) Which electrode is negatively charged?
- (ii) The carriers of the current in the cell
- (iii) Individual reaction at each electrode.
- **7.** Explain why?
 - (i) Reaction $FeSO_4$ (aq) + Cu (s) \rightarrow CuSO₄ (aq) + Fe does not occur.
 - (ii) Zinc can displace copper from aqueous CuSO₄ solution but Ag cannot.
 - (iii) Solution of $AgNO_3$ turns blue when copper rod is immersed in it.

5 - Mark Questions

- 1. (i) MnO₄²⁻ undergoes disproportionation reaction in acidic medium but MnO₄⁻ does not. Give reason.
 - (ii) Give one example each of the following redox reactions:
 - (a) Combination reaction

- (b) Decomposition reaction
- (c) Metal displacement reaction
- 2. Consider the cell reaction of an electrochemical cell : Ni(s) + 2 Ag⁺(aq) \rightarrow Ni²⁺ (aq) + 2 Ag (s) and answer the following questions :
 - (i) Write anode and cathode half reactions.
 - (ii) Mention the direction of flow of electrons.
 - (iii) How is the electrical neutrality maintained in the solutions of the two half cells.
 - (iv) Write the formula for calculating standard emf of this cell.
 - (v) How does the emf change when the concentration of silver ions is decreased?
- **3.** Justify the reason that following reactions are redox reactions.
 - (a) $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$
 - (b) $\operatorname{Fe_2O_3} + 3\operatorname{CO}(g) \longrightarrow 2 \operatorname{Fe}(g) + 3\operatorname{CO_2}(g)$
 - (c) $NH_3(g) 5O_2(g) \longrightarrow 4NO(g) + 5H_2O(g)$
 - (d) $BCl_3(g) + 3 LiAlH_4 \longrightarrow B_2H_6 + LiCl + AlCl_3$
 - (e) $2K + F_2 \longrightarrow 2KF$
- [Hints:- CuO is oxidizing agent, H_2 is acting as reducing agent because Cu (II) is changing to Cu (0) by gain of e^-H_2 is getting oxidised to H_2O (g), its oxidations sate is changing from 0 to +1, by loss of electrons.
 - (ii) It is redox reaction: Fe₂O₃ is getting reduced to fe. CO is getting oxidised to CO₂.]
- **4.** Using standard electrode: Predict if the reaction between as the following is feasible.
 - (i) Fe^{3+} (aq) and I^- (aq)
 - (ii) Ag⁺ and Cu
 - (iii) Fe³⁺ and Br⁻ (aq)
 - (iv) Ag and Fe^{3+} (aq)
 - (iv) Br_2 (aq) and Fe^{2+} (aq)
- **Hint:** $E^{\theta}_{I_2/\Gamma}$ = 0.541 V, $E^{\theta}_{Cu^{2^+/Cu}}$, = 0.34V, $E^{\theta}_{Br_2/Br^-}$ = 1.09V, $E^{\theta}_{Ag^+/Ag}$ = 0.80V, $E^{\theta}_{Fe^{3^+/Fe^{2^+}}}$ = 0.77V.
- **5.** Draw the diagram for the galvanic cell which would have overall chemical reaction as

$$Zn + 2Ag+ \longrightarrow Zn^{2+} + 2Ag.$$

Answer the following:

- (i) Write the reactions occurring at each electrode.
- (ii) In which directions do the electrons flow in the external circuit?
- (iii)Name the salt to be taken in salt bridge.
- (iv)Label the anode and cathode.
- (v) How does the EMF change when the concentration of solvers ions is decreased?





Hydrogen

- Hydrogen is the first element in the periodic table and also the lightest element known. Electronic configuration of Hydrogen is 1s¹.
- Isotopes of hydrogen:
 - (i) Protium (₁¹H)
 - (ii) Deuterium (₁²H or ₁²D)
 - (iii) Tritium ($_{1}^{3}$ H or $_{1}^{3}$ T)
- Preparation of Dihydrogen:
 - (i) Laboratory preparation : $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$.
 - (ii) Commercial preparation: By electrolysis of acidified water.
 - (iii) High purity dihydrogen is obtained by electrolysing warm aqueous barium hydroxide.

• Properties :

- * Reaction with halogen: $H_2 + X_2 \longrightarrow 2HX$ [X = F, Cl, Br, I]
- * Reaction with oxygen: $H_2(g) + O_2(g) \xrightarrow{\Delta} 2H_2O(l) \Delta H^{\varnothing}$ = $-285.9 \text{ kJ mol}^{-1}$
- * Reaction with nitrogen: $3H_2(g) + N_2(g) \xrightarrow{\Delta} 2NH_3(g) \Delta H^{\sigma}$ = -92 kJ mol^{-1}
- * Reaction with alkali metals: $H_2(g) + 2M(g) \xrightarrow{\Delta} 2MH(s)$ It is relatively inert at room temperature due to the high H-H bond enthalpy.
- Uses of Dihydrogen:
 - (i) For synthesis of Ammonia (NH₃)

- (ii) For production of Methanol (CH₃OH)
- (iii) In oxyhydrogen torches
- (iv) In a fuel cell.

Hydrides

- (i) **Ionic or salt like or saline hydrides** are formed with most of the s-block elements. Significant covalent character is found in LiH, BeH₂ and MgH₂.
- (ii) **Covalent or Molecular hydrides** are formed with most of the *p*-block elements. There are further classified as:
- (a) **Electron deficient hydrides** are formed by group 13 elements e.g., B_2H_6 . They acts as Lewis acid.
- (b) **Electron Precise hydrides** are formed by group 14 elements e.g., CH_4 .
- (c) **Electron rich hydrides** have lone pair of electrons on central atoms of the molecules. Elements of group 15-17 form these types of hydrides.

NH₃, HF has high m.p./b.p. due to presence of intermolecular hydrogen bonding.

- (iii) **Metallic or Non-stoichiometric or Interstitial hydrides** are formed by d and f-block elements. For example La $H_{2.87}$ or $NiH_{0.6-0.7}$.
- **Water**: (H₂O)

Hard water: Hard water contains calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate. Hard water does not give lathers with soap.

Soft water: Water free from soluble salts of calcium and magnesium is soft water.

Types of Hardness:

Temporary hardness is due to presence of calcium or magnesium hydrogen carbonate in water.

Temporary hardness can be removed by:

- (i) Boiling
- (ii) Clark's Method

Permanent hardness:

Such hardness is due to presence of calcium or magnesium chlorides and sulphates.

Permanent hardness can be removed by:

- (i) Treatment with washing soda
- (ii) Calgon's method
- (iii) Ion exchange method.

Demineralised or Deionised water: Water free from all soluble mineral salts is known as **demineralised water.**

Hydrogen Peroxide (H₂O₂)

Preperation:

- (i) By electrolytic oxidation of acidified sulphate solutions at high current density.
- (ii) 2-Ethylanthraquinol $\stackrel{O_2 \text{ (air)}}{\longleftarrow H_2/Pd}$ H_2O_2 + (oxidised product)

Physical Properties

- (i) Miscible with water in all proportions.
- (ii) A 30% of H₂O₂ solution is marked as <u>'100 volume' hydrogen peroxide</u>.

• Chemical Properties:

- (i) It acts as an oxidising as well as reducing agent.
- (ii) Oxidising action in acidic medium:

$$2Fe^{2+}(aq) + 2H^{+}(aq) + H_2O_2(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$$

(iii) Reducing action in acidic medium:

$$2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + SO_2$$

• Storage of H₂O₂:

- (i) Stored in wax-linked glass or plastic vessels in dark. Urea can be added as a stabiliser.
- (ii) It is kept away from dust because dust can induce explosive decomposition of the compound.

• Uses of H_2O_2 :

- (i) As an antiseptic it is sold in the market name **perhydrol**.
- (ii) In synthesis of hydroquinone.
- (iii) As a bleaching agent.

 Auto-protolysis of water: Water accepts a proton from other water molecule to from H₃O⁺ and OH⁻ this porous is called auto – protolysis of water

$$H_2O(1) + H_2O(1) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Its significance is that water can act as acid as well as base i.e. it is amphoteric in nature.

- 2. Hydrogen economy:—It is transportation and storage of energy in the form of liquid or gaseous hydrogen. Advantage of hydrogen economy is that energy is transmitted in the form of dihydrogen and not as electric power
- **3. Hydrogenation:**—It is a process of converting polyunsaturated oils in edible fats.

Vegetable oil +
$$H_2 \frac{Ni}{473K}$$
 Vanaspati ghee (fat).

4. Syngas:—It is a mixture of CO and H₂ in 1:1 ratio and also known as water gas or syntnesis gas.

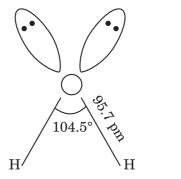
$$C(s) + H_2O(g) = \frac{1270 \text{ K}}{\text{Ni}} CO_2 + H_2(g)$$

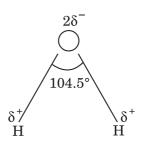
Carbon Carbon monoxide

5. Water gas shift reaction.

$$CO + H_2O \frac{673 \text{ K}}{\text{iron chromate as catalyst}} CO_2 + H_2$$

- **6. Full-cell:**—Fuel cell is a cell in which chemical energy of fuel is converted into electrical energy.
- 7. Structure of water:— It is bent molecule in gas phase with HOH bond angle 104.5° and O–H bond length of 95.7 pm as shown if figure





Chemistry Class XI

- **8.** Calgon:— It is sodium polymetaphosphate (NaPO₃)_n it is used to remove. Permanent hardness of water.
- **9. De-ionized water:** Pure di-mineralised (ionized water) free from all soluble mineral matter is obtained by passing water successively through a cation exchanger (in the H⁺ form) and an anion exchanger for removal by cation and anions

$$2RH + M^{2+} \longrightarrow MR_2 + 2H^+$$
(R is the resin anion M^{2+} is cation)
$$RNH_2 + H_2O \longrightarrow RNH_3^+, OH^-$$

$$RNH_3^+ + OH^- + X^- \longrightarrow RNH_3^+, X^- + OH^-$$

$$H^+ + OH^- \longrightarrow H_2O$$

- 1. Name the isotope of hydrogen which is radioactive in nature. [Ans. Tritium]
- 2. H⁺ ions does not exist freely and is always associated with other atoms or molecule. Explain.
- 3. Give the composition of water gas. $[Ans. CO, H_2]$
- **4.** Name the compound whose electrolysis in aqueous state, give high purity (99.95%) dihydrogen. [Ans. aq Ba(OH)₂ solution]
- 5. Give the main purpose of water gas shift reaction.
- **6.** Write the chemical reaction occuring during coal gasification.
- 7. Name the element used in fuel cell for generating electricity. [Ans. H_2]
- **8.** Give an example of electron deficient covalent hydride. [Ans. B_2H_6]
- 9. Name the hydrides which have high potential for hydrogen storage.

[Ans. Metallic hydrides]

10. Name the groups in *d*-block elements which do not form metallic hydrides.

[Ans. 7, 8, 9]

- 11. H₂ is relatively inert at room temperature. Explain.
- 12. Complete the reaction:

$$C(s) + H_2O(g) \xrightarrow{1270 \text{ K}} (A) \underline{\qquad} (g) + (B) \underline{\qquad} (g).$$
 [Ans. CO, H₂]

- 13. Name the phenomenon as a reason of which water has unusual boiling point.[Ans. Extensive hydrogen bonding]
- 14. Draw structure of water.
- **15.** At atmospheric pressure ice crystallised in the form but at very low temperature it condenses to form. [Ans. Hexagonal, cubic]
- **16.** Mention the temperature at which density of ice is maximum.[Ans. 4°C]
- 17. Density of ice is than density of liquid water. [Ans. Less]
- **18.** Complete the reaction:

$$2H_2O(l) + 2Na(s) \longrightarrow$$

- **19.** How many hydrogen-bonded water molecules (s) are associted in $CuSO_4.5H_2O$. [Ans. One]
- **20.** Name the compound used in Clark's method to remove temporary hardness of water. [Ans. Lime]
- 21. Write the chemical formula of "Calgon". [Ans. Na₄P₆O₁₈]
- 22. A 30% solution of H₂O₂ is marketed as volume.[Ans. 100 volume]
- 23. Draw gas phase structure of H_2O_2 .
- **24.** Name the organic compound whose auto-oxidation is used to produce H_2O_2 commercially or industrially. [Ans. 2-Ethylanthraquinol]
- 25. How is heavy water obtained from ordinary water?

1. Complete the following reactions:

(i)
$$CO(g) + H_2(g) \xrightarrow{\Delta} Catalyst$$

(ii)
$$Zn(s) + NaOH(aq) \xrightarrow{\Delta}$$

- **2.** Among NH₃, H₂O and HF which would you except to have highest magnitude of hydrogen bonding and why?
- **3.** How do you except the metallic hydrides to be useful for hydrogen storage? Explain.
- **4.** How can the production of dihydrogen obtained from "Coal gasification" be increased?
- **5.** Write the name of isotopes of hydrogen. What is the mas ratio of these isotopes?
- **6.** Complete the reactions :

(i)
$$CO(g) + 2H_2(g) \xrightarrow{Cobalt} Catalyst$$

(ii)
$$CH_4(g) + H_2O(g) \xrightarrow{1270 \text{K}}$$

- 7. Comment on the reactions of dihydrogen with:
 - (i) Chlorine, (ii) Sodium.
- **8.** Arrange the following:
 - (i) LiH, NaH, CsH (In increasing order of ionic character)
 - (ii) H—H, D—D, F—F (In decreasing order of bond dissociation enthalpy)
- **9.** List two uses of dihydrogen.
- **10.** Complete the reactions :

(i)
$$H_2 + CO + RCH = CH_2 \longrightarrow$$

(ii)
$$H_2 + RCH_2CH_2CHO \longrightarrow$$

- 11. Give two reactions to show amphoteric nature of water.
- **12.** Complete the reactions :

(i)
$$2F_2(g) + 2H_2O(l) \longrightarrow$$

(ii)
$$6\text{CO}_2(g) + 12\text{H}_2\text{O}(l) \longrightarrow$$

- 13. What is the difference between the term hydrolysis and hydration.
- **14.** What do you understand by term 'autoprotolysis' of water ? What is its significance ?

- **15.** What causes the temporary and permanent harness of water?
- **16.** Is demineralised or distill water useful for drinking purposes? If not, how can it be made useful?
- **17.** Explain the terms : (i) Hydrogen economy. (ii) Fuel cell.
- **18.** Write chemical reactions to justify that hydrogen peroxide can function as an oxidising as well as reducing agent.
- **19.** Compare the structure of H_2O and H_2O_2 .
- **20.** How does H_2O_2 behaves as a bleaching agent?
- **21.** H₂O₂ acts as an oxidizing as well as reducing agent. Why?

- **1.** Complete the chemical reactions :
 - (i) $8LiH + Al_2Cl_6 \longrightarrow$
 - (ii) $2\text{LiH} + \text{B}_2\text{H}_6 \longrightarrow$
- 2. What do you understand by : (i) Electron deficient, (ii) Electron precise, (iii) Electron rich compounds of hydrogen ? Provide justifications with suitable examples.
- **3.** What do you understand by the term "non-stoichiometric hydrides"? Do you expect this type of the hydrides to be formed by alkali metals. Explain and Justify your answer.
- **4.** Arrange the following:
 - (i) CaH₂, BeH₂, TiH₂ (in order of increasing electrical conductance)
 - (ii) NaH, MgH₂, H₂O (in order of increasing bond dissociation enthalpy)
 - (iii) Li, F, H (in order of increasing ionisation enthalpy)
- 5. What do you understand by the terms:
 - (i) Syn gas (ii) Water gas shift reaction (iii) Producer gas.
- **6.** Would gas except the hydrides of N, O and F to have lower boiling point than the hydrides of their subsequent group members? Give reasons.
- 7. Can phosphorous with outer electronic configuration $3s^23p^3$ form PH₅? Explain.

- 8. Why and how the hydrogen is regarded as a fuel of future? Explain.
- **9.** Write the reactions when dihydrogen reacts with (i) O₂ (ii) N₂ (iii) Cl₂ under specific conditions.
- **10.** Name the hydrides:
 - (i) Which is non stoichiometric in nature?
 - (ii) Which are stoichiometric compounds?
 - (iii) Which has electron rich type hydrides?
- 11. Complete the reactions:

(i)
$$CaO(s) + H_2O(g) \longrightarrow$$

(ii)
$$AlCl_3(g) + H_2O(l) \longrightarrow$$

(iii)
$$Ca_3N_2(s) + H_2O(l) \longrightarrow$$

- **12.** Discuss the principle and method of softening of hard water by synthetic exchange of resin method.
- 13. What is meant by 'demineralised' water and how can it be obtained?
- **14.** What properties of water make it useful as a solvent? What types of compound can it (i) dissolved (ii) hydrolyse?
- **15.** Calculate the strength of 10 volume solution of H₂O₂.
- **16.** Complete the reactions :

(i)
$$2Fe^{2+}$$
 (aq) + $2H^{+}$ (aq) + H_2O_2 (aq) \longrightarrow

(ii)
$$HOC1 + H_2O_2 \longrightarrow$$

(iii)
$$Mn^{2+} + H_2O_2 \longrightarrow$$

- 17. Give three uses of H_2O_2 .
- **18.** Complete the reactions:

(i)
$$CaC_2 + 2D_2O \rightarrow$$

(ii)
$$SO_3 + D_2O \rightarrow$$

(iii)
$$Al_4C_3 + 12D_2O \rightarrow$$

- **19.** Give the limitations of using H_2 as a fuel.
- **20.** H_2O_2 is stored in a wax lined glass or plastic vessels. Explain an equation showing decomposition of H_2O_2 on exposure to light.

- 1. Answer the following:
 - (a) Name the most abudant form of hydrogen isotope.

[Ans. ${}_{1}^{1}H$]

(b) Name the particles emitted by tritium.

[Ans. β^-]

- (c) Mixture of CO and H₂ is used for preparation [Ans. Methanol]
- (d) Name the catalyst used in Haber's Process for manufacture of $NH_3(g)$.

[Ans. Fe]

(e) Name two electron rich hydrides.

[Ans. NH_3 , H_2O]

- **2.** Answer the following:
 - (a) During Clark's method. Name the compound in which Mg is precipitated out. [Ans. Magnesium Hydroxide]
 - (b) Give the formula of Zeolite used in ion exchange method to remove permanent hardness of water. [Ans. NaAlSiO₄]
 - (c) Complete the reaction:

$$BaO_2.8H_2O(s) + H_2SO_4(aq) \rightarrow$$

- (d) H₂O₂ is miscible with water. Assign reason.
- (e) Name the compound when can be used as a hair beach, mild antiseptic in the form of perhydrol. [Ans. H_2O_2]
- 3. 1. Complete the following chemical equations

2.
$$_$$
 + water \longrightarrow CaCO₃ + NH₃ (Ammonia)

3. _____ + Hydrogen peroxide
$$\xrightarrow{H^+}$$
 CrO₅+ _____

4.
$$Na_2O + H_2O \longrightarrow$$

5.
$$D_2O + Na_3A_S \longrightarrow$$

Hints (i) $CaNCN. + 3H_2O \longrightarrow CaCO_3 + 2NH_3$

(ii)
$$Al_4C_3 + H_2O \longrightarrow 4Al (OH)_3 + 3CH_4$$

(iii)
$$Cr_2O_7^{2-} + 4H_2O_2 \xrightarrow{H^+} 2CrO_5 + 5H_2O$$

(iv)
$$Na_2O + H_2O \longrightarrow 2NaOH$$

(v)
$$3D_2O + Na_3A_S \longrightarrow 3NaOD + A_SD_3$$

4. Describe the usefulness of water in biosphere and biological systems.





$lue{}$ Chapter - 10

s-Block **Elements**

- *s*-block elements consists of group-I (Alkali metals) and group-2 (Alkaline earth metals).
- Group 1st elements—Li, Na, K, Rb, Cs, Fr.
- Group 2nd elements—Be, Mg, Ca, Sr, Ba, Ra.
- **Atomic radius**—Atomic radius of alkali metals are greater than alkaline earth metals.
- **Hydration enthalpy:** Decreases with increases in ionic sizes.
- **Ionic mobility**: Smaller the size of ion, more highly it is hydrated and hence lower is its ionic mobility.

$$Li^+\!<\!Na^+\!<\!K^+\!<\!Rb^+\!<\!Cs^+$$

- **Ionisation enthalpies :** 1st I.E. of group 1st is smaller than group 2nd elements but 2nd I.E. of group 2nd is smaller than group 1st elements.
- **Flame colouration :** Due to low I.E., *s*-block elements and their salts imparts characteristics colour of oxidising flame (except Be and Mg). Be and Mg do not show flame colouration because they have small size and very high ionisation enthalpy.
- **Reducing character:** Due to large negative electrode potentials alkali metals are stronger reducing agent than alkaline earth metal.
- Reactivity towards air :

$$4Li + O_2 \longrightarrow 2Li_2O$$
 (Lithium oxide)

$$2Na + O_2 \longrightarrow Na_2O_2$$
 (Sodium peroxide)

$$M + O_2 \longrightarrow MO_2$$
 (M = K, Rb, Cs metal superoxide)

Alkaline earth metals being smaller in size do not from superoxides.

• Reactivity towards H₂O:

$$2M + 2H_2O \longrightarrow 2MOH + H_2$$

(Alkali metal)

$$M + 2H_2O \longrightarrow M(OH)_2 + H_2$$

(Alkaline earth metals)

• Reactivity towards hydrogen:

$$2M + H_2 \longrightarrow 2MH$$

 $(M = Li, Na, K, Rb, Cs)$
 $M + H_2 \longrightarrow MH_2$
 $(M = Mg, Ca, Sr, Ba)$
 $2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$.

• Reactivity towards halogens:

$$2M + X_2 \longrightarrow 2MX (M = Li, Na, K, Rb, Cs)$$

 $M + X_2 \longrightarrow MX_2 (M = Mg, Ca, Sr, Ba)$
 $BeO + C + Cl_2 \xrightarrow{600-800 \text{ K}} BeCl_2 + CO$

- Solution in liquid ammonia: The fresh solution of alkali metals and alkaline earth metals (except Be and Mg) is deep blue, paramagnetic and highly reducing due to presence of ammoniated electrons.
- Solubility of alkaline earth metal carbonate in water :

$$Li_2CO_3 < Na_2CO_3 < K_2CO_3 < RbCO_3 < Cs_2CO_3$$

• Solubility of alkaline earth metal carbonates in water.

$$BaCO_3 \le SrCO_3 \le CaCO_3 \le MgCO_3 \le BeCO_3$$

• Solubility of alkaline earth metal sulphates in water :

$${\rm BaSO_{4}} < {\rm SrSO_{4}} < {\rm CaSO_{4}} < {\rm MgSO_{4}} < {\rm BeSO_{4}}$$

• Thermal stability of alkali metal carbonates:

$${\rm Li_2CO_3} < {\rm Na_2CO_3} < {\rm K_2CO_3} < {\rm Rb_2CO_3} < {\rm Cs_2CO_3}$$

• Thermal stability of alkaline earth metal carbonates:

$$BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$$

- **Anamolous behaviour of Li and Be :** It is due to very small size, high I.E. and high polarising power (*i.e.*, charge/radius)
- Diagonal relationship (similarities) between Li and Mg:
 - (i) Both Li and Mg are hard.
 - (ii) Both react with N₂ to form nitrides.

$$6Li + N_2 \longrightarrow 2Li_3N$$

 $3Mg + N_2 \longrightarrow Mg_3N_2$

(iii) Decomposition of carbonates:

$$Li_{2}CO_{3} \longrightarrow Li_{2}O + CO_{2}$$

$$MgCO_{3} \stackrel{\Delta}{\longrightarrow} MgO + CO_{2}$$

- (iv) Both LiCl and ${\rm MgCl_2}$ are deliquescent. They form hydrates salts LiCl.2H₂O and ${\rm MgCl_2.6H_2O}$.
- (v) **Decomposition of nitrates:**

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$
$$2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$$

- Diagonal relationship (similarities) between Be and Al:
 - (i) Both are passive to acids due to formation of oxide layer.
 - (ii) Hydroxides of both dissolve in alkali to form $[Be(OH)_4]^{2-}$ and $[Al(OH)_4]^{-}$.
 - (iii) Chloride of both has bridged structure.
 - (iv) Both have tendency to form complexes of BeF_4^{2-} , AlF_6^{3-} .
- Manufacturing of washing soda (Na₂CO₃.10H₂O):

Solvay process:

$$\begin{aligned} &\mathrm{NH_3}(g) + \mathrm{CO_2}(g) + \mathrm{H_2O}\ (l) \longrightarrow \mathrm{NH_4HCO_3}\ (\mathrm{aq}) \\ &\mathrm{NH_4HCO_3}\ (\mathrm{aq}) + \mathrm{NaCl}\ (\mathrm{aq}) \longrightarrow \mathrm{NaHCO_3}(\mathrm{s}) + \mathrm{NH_4Cl}\ (\mathrm{aq}) \\ &\mathrm{2NaHCO_3} \stackrel{\Delta}{\longrightarrow} \mathrm{Na_2CO_3} + \mathrm{H_2O}(l) + \mathrm{CO_2}(g) \\ &\mathrm{2NH_4Cl}\ (\mathrm{aq}) + \mathrm{Ca}(\mathrm{OH})_2 \to \mathrm{CaCl_2}(\mathrm{s}) + 2\mathrm{H_2O}(l) + 2\mathrm{NH_3}\ (g) \end{aligned}$$

• Manufacturing of caustic soda (NaOH): Castner-Kellner cell.

Cathode: Na⁺ +
$$e^- \xrightarrow{\text{Hg}}$$
 Na-Hg

Anode: Cl⁻ $\longrightarrow \frac{1}{2}$ Cl₂ + e^-

2Na-Hg + 2H₂O \longrightarrow 2NaOH + 2Hg + H₂

• Plaster of paris: (CaSO₄.½H₂O)

$$2(CaSO_4.2H_2O) \xrightarrow{\Delta} 2(CaSO_4).H_2O + 3H_2O$$

Gypsum

 Cement is a finely powdered mixture of calcium silicates and aluminate along with small quantities of gypsum which sets into a hard stone like mass when treated with water.

1 - Mark Questions

- 1. What is the oxidation state of K in KO₂?
- 2. Why are group I element called alkali metals?
- **3.** Potassium carbonate cannot be prepared by solvay process. Why?
- **4.** LiCl is soluble in organic solvent. Why?
- 5. Why are group I elements called alkali metals?
- **6.** Alkali metals are strong reducing agents. Why?
- 7. Why do alkali metals give characteristics flame colouration?
- 8. Arrange the following in order of increasing covalent character : MCl, MBr, MF, MI (where M = Alkali metal) [Ans. MF < MCl < MBr < MI]
- 9. Alkali metals can not be obtained by chemical reduction method. Explain.
- **10.** Why is sodium metal kept under kerosene oil?
- 11. Why Be and Mg do not give characteristics colour to the flame?
- **12.** Arrange the alkaline earth metal carbonate in the decreasing order of thermal stability.
- **13.** Why do alkaline earth metals not form any superoxide?
- **14.** Why gypsum is added to cement?
- 15. How plaster of paris is obtained from gypsum?
- **16.** BeO is insoluble in water but BeSO₄ is soluble in water? Why?
- **17.** Why second I.E. of group II elements is less than group I elements?
- **18.** What is quick lime? How is it prepared?
- **19.** Why does Be shows similarities with Al?
- **20.** Name the alkaline earth metal hydroxide which is amphoteric.

- 1. Why are alkali metals soft and have low melting points?
- 2. Write any four similarities between Li and Mg.
- **3.** Why are potassium and caesium rather than Lithium used in photoelectric cells?
- **4.** Why is Li₂CO₃ decomposed at a lower temperature whereas Na₂CO₃ at higher temperature?
- 5. Among the alkali metals which has:
 - (i) Highest melting point.
 - (ii) Most electropositive character
 - (iii) Lowest size of ion.
 - (v) Strongest reducing character. [Ans. (i) Li (ii) Cs (iii) Li (iv) Li]
- **6.** Why does the solubility of alkali earth metal carbonates and sulphates decreases down the group?
- 7. Draw the structure of BeCl₂ in (i) Vapour phase (ii) Solid state.
- **8.** When CO₂ gas is passed in lime water it turns milky but in case of excess CO₂ milkiness disappears. Support the statement by giving suitable reaction equations.
- 9. (i) E^{θ} for M^{2+} (aq) $+ 2e^{-} \longrightarrow M(s)$ (where M = Ca, Sr, Ba) is nearly constant.
 - (ii) What is dead burnt plastar? How is it obtained from gypsum?
- 10. Write two important uses of (i) Limestone (ii) Quick lime.

3 - Mark Questions

- 1. Assign reason for the following:
 - (i) Compounds of lithium are generally covalent.
 - (ii) Alkali metals are strong reducing agent.
 - (iii) LiCl is more covalent than NaCl.
- 2. Discuss the various reactions that occur in Solvay process.

- **3.** Explain why?
 - (i) Lithium salts are commonly hydrated.
 - (ii) Sodium peroxide is widely used as as oxidising agent.
 - (iii) Sodium wire is used to remove moisture from benzene but can't be used for drying alcohol.
- **4.** Sodium hydroxide is generally prepared by electrolysis of brine solution in the Castner-Kellner cell :
 - (i) Write the reactions that occur in the cell.
 - (ii) Write any two uses of NaOH.
- **5.** Explain with suitable reasons :
 - (a) A solution of Na₂CO₃ is alkaline.
 - (b) Alkali metals are prepared by electrolysis of their fused chlorides.
 - (c) Sodium is found to be more useful than potassium?
- **6.** Arrange the following in order of property mentioned against each :
 - (i) BaCl₂, MgCl₂, BeCl₂, CaCl₂ (Increasing ionic character)
 - (ii) Mg(OH)₂, Sr(OH)₂, Ba(OH)₂, Ca(OH)₂ (Increasing solubility in water)
 - (iii) BeO, MgO, BaO, CaO (Increasing basic strength)
- 7. What happens when:
 - (i) Mg is burnt in air.
 - (ii) Quick lime is heated with silica.
 - (iii) Chlorine is heated with slaked lime.
- **8.** Write the raw material required for the manufacture of portland cement? Why gypsum is added into it.
- **9.** (i) Why alkaline earth metals cannot be obtained by reduction of their oxide?
 - (ii) Why the elements of group 2 are known as alkaline earth metals?
- 10. (i) Alkaline earth metals forms ionic salt having bivalent cations. Explain. Why?
 - (ii) A piece of magnesium ribbon continues to burn in SO₂. Why?

- 1. Explain the following observation:
 - (a) LiI is more soluble than KI in ethanol.
 - (b) Sodium reacts with water less vigorously than potassium.
 - (c) LiF is insoluble in water.
 - (d) The mobilities of the alkali metal ions in aqueous solution are $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.
 - (e) Lithium is the only alkali metal to form a nitride directly.
- 2. Complete the following reaction equations:

(i) BeCl₂ + LiAlH₄
$$\rightarrow$$

(ii) CaO + SiO₂
$$\rightarrow$$

(iii)
$$Ca(OH)_2 + Cl_2 \rightarrow$$

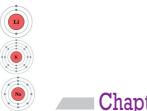
(iv) CaO +
$$P_4O_{10} \rightarrow$$

(v)
$$Ca(OH)_2 + CO_2 \rightarrow$$

3. Compare the solubility and thermal stability of the following :

Compounds of the alkali metals with those of alkaline earth metals (a) nitrates (b) carbonates (c) sulphates.

- **4.** Explain the significance of Sodium (Na), Potassium (K), Magnesium (Mg) and Calcium(Ca) in biological fluids.
- **5.** Explain the significance of Sodium Potassium, Magnesium and Calcium biological fluids.
- **6.** (i) A solutions of Na₂CO₃ is alkaline why?
 - (ii) BeO insoluble but BeSO₄ in soluble in water. Why?
 - (iii) Lithium salts are commonly hydrated and those of other alkali metal ions are usually anhydrous give reasons.
 - (iv) What is the importance of cement.
 - (v) What happen when quick lime is heated with silica.



Chapter - 11

p-Block **Elements**

General outer Electronic configuration : ns^2np^{1-6} .

Inert Pair Effect:

- Reluctance of ns^2 electrons of valence shell to participate in bond formation is termed as inert pair effect.
- It arises due to poor or insufficient shielding of *ns*² electrons by intervening d- or f-electrons & hence increases down the group.

Causes of Anomalous Behaviour of First Element in groups of p-Block:

- (i) Very small size
- (ii) Unavailability of vacant d-orbital
- (iii) Tendency to form $p_{\pi} p_{\pi}$ multiple bonds.

Group No-13 Elements: (B, Al, Ga, In, Tl, Nh)

- General Electronic Configuration: ns² np¹
- **Atomic radius:** B < Ga < Al < In <TI

 $r_{Ga} < r_{Al}$ due to ineffective shielding of valence electrons by intervening 3d-electrons in Ga.

- Ionization Enthalpies: : B > T1 > Ga > A1 > In
- Electronegativity: B > Tl > In > Ga > Al
- Oxidation States: B (+3), Al (+3), Ga (+3, +1), In (+3, +1), Tl (+1, +3)
 Tl (+1) is more stable than Tl (+3) due to inert pair effect.

- Nature of Compounds: Compounds of group 13 elements are electron deficient i.e. Lewis Acid and hence used as industrial catalyst e.g. BF₃, AlCl₃.
- Halides: MX₃ type, Electron deficient (Lewis acid), AICI₃ exist as dimer
- **Borax:** $Na_2B_4O_7.10H_2O$. On heating it form transparent glassy bead consisting of $NaBO_2 + B_2O_3$.
- Boric acid: H₃BO₃, It acts as a Lewis acid by accepting electron pair from OH⁻ ions of water.
- Diborane: B₂H₆, Colourless & toxic gas, acts as Lewis acid due to having electron deficient 3c-2e⁻ bonds. Obtained by treating BF₃ with LiAIH₄ or NaH, Also obtained by treating NaBH₄ with l₂.
- Borazine: B₃N₃H₆, It is isostructural with benzene and hence known as inorganic benzene. Prepared by heating B₂H₆ withNH₃

Group -14 Elements: (C, Si, Ge, Sn, Pb,Fl)

- General Electronic Configuration: ns² np²
- Atomic radius: C < Si < Ge < Sn < Pb
- **lonisation Enthalpy:** LiH_x : C > Si > Ge > Sn < Pb
- Oxidation States: C (+4), Si (+4), Ge (+4, +2), Sn (+4, +2), Pb (+4, +2)
 Pb (+2) is more stable than Pb (+4) due to inert pair effect.
- Oxides: Form di oxides (MO₂) & mono oxides (MO).
 - ${\rm PbO_2}$ is powerfull oxidizing agent because Pb stabilizes in +2 oxidation state due to inert pair effect. ${\rm CO_2}$ is gas while ${\rm SiO_2}$ is network solid because C has ability to form $p_\pi p_\pi$ multiple bonds.
- **Halides:** Form tetra halides (MX_4) & dihalides (MX_2) .

Tetra halides are more covalent due to greater polarizing power of cation.

 ${\rm CCI}_4$ is not hydrolysed with water as C has no vacant d-orbital to accept electron pair from water.

- Catenation: $C \gg Si \gg Ge \approx Sn \gg Pb$
- Allotrops of carbon: Diamond (sp³), Graphite (sp²), Fullerenes (sp²)
- Silicones: Silicones are synthetic organosilicon compounds containing R₂SiO repeating units. Silicones are water repellent, heat resistant, chemically inert, electrical insulators, resistant to oxidation.
- Silicates: Silicates are compounds in which anions are derived from Si-o-si- tetrahedral units.
- **Zeolites:** Zeolites are 3D silicates in which some of the Si atoms are replaced by Al³⁺ ions and negative charge is balanced by cations such as Na⁺, K⁺, Ca²⁺ etc.
- ZSM-5 is used in petrochemical industries to convert methanol into petrol.

Group - 15 Elements: (N, P, As, Sb, Bi, Mc)

- General Electronic Configuration: ns² np³
- Atomic radius: $N < P < A_S < Sb < Bi$
- **lonisation Enthalpy:** $\Delta_i H_1$: N > P > As > Sb > Bi
- Oxidation States: N (+5, +3), P (+5,+3), As (+5, +3), Sb (+5,+3), Bi (+5, +3) Bi (+3) is more stable than Bi (+5) due to inert pair effect.
- Oxides: Form trioxides (M₂O₃) & pentaoxides (M₂O₅).
- Halides: Form trihalides (MX₃) & pentahalides (MX₅).
 Nitrogen does not form penta halides because it cannot extend its covalency beyond four due to absence of vacant d-orbitals.

Pentahalides are more covalent than trihalides due to greater polarizing power of cation.

• Hydrides: MH₃ type, Lewis base, pyramidal structure

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

(Basic character, Bond angle & Thermal Stability)

$$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$$

(Reducing Character) PH₃< AsH₃< NH₃< SbH₃< BiH₃ (Boiling point)

- Oxides of Nitrogen: Nitrogen having ability to form $p_{\pi} p_{\pi}$ multiple bonds can form oxides in all oxidation states from +1 to +5 i.e. N₂O, NO,N₂O₃, NO₂,N₂O₄ & N₂O₅
- **Dinitrogen** (N₂): Much less reactive due to high bond enthalpy of N=N. Prepared by heating $(NH_4)_2Cr_2O_7$ or a solution of $NH_4Cl + NaNO_2$.
- Ammonia (NH₃): Pungent & irritating smell gas. It is prepared on commercial scale by Haber's process. NH₃ acts as Lewis base /Ligand / complexing agent due to the presence of electron pair on N atom.
- Nitric acid (HNO₃): It is very powerfull oxidizing agent because it readily gives nascent oxygen both in concentrated or dilute form. Concentrated HNO₃ oxidizes non-metals to their oxoacids and metals to their nitrates.
- **Allotropes of Phosphorous:** White (Most reactive due to angular strain), Red & Black phosphorous.
- **Phosphine** (PH₃): Poisonous gas with rotten fish smell, it is prepared by heating white phosphorous with concentrated. NaOH in inert atmosphere of CO₂. Phosphine can also be prepared by dropping H₂O or HCI on Ca₃P₂.
- **Phosphorous trichloride (PCl₃):** Colourless liquid, fumes in moisture due to the formation of HCI.
- **Phosphorous pentachloride** (PCl₅): In gaseous state it is covalent (trigonal bipyramid) but in solid state it is ionic i.e. [PCl₄]⁺[PCl₆]⁻.
- Oxoacids of Phosphorous:
 - (i) Hypophosphorous acid (H₃PO₂): Monobasic, reducing
 - (ii) Phosphorous acid (H₃PO₃): Dibasic/reducing
 - (iii) Phosphoric acid (H₃PO₄): Tribasic, Non-reducing
 - (iv) Hypophosphoric acid (H₄P₂O₆): Tetrabasic, non-reducing A
 - (v) Pyrophosphoric acid (H₄P₂O₇): Tetrabasic, non-reducing

- 1. Mention two important ores of boron?
- 2. Name the elements of group 13 which forms only covalent compounds?
- **3.** Why the atomic radius of gallium is less than that of Al?

- 4. Why does Boron forms electron deficient compounds?
- **5.** Boron does not exist as B^{3+} ion. Why?
- **6.** Why the trihalide of group 13 elements fume in moist air?
- 7. Aluminium form $[AlF_6]^{3-}$ but boron does not form $[BF_6]^{3-}$.
- **8.** Why boric acid is a monobasic acid?
- **9.** White fumes appear around the bottle of anhydrous AlCl₃. Give reason.
- 10. AlCl₃ exist as dimer while BCl₃ exist as monomer, why?
- 11. Mention the type of hybridization of Boron in B_2H_6 . [Ans. sp^3]
- 12. Write the formula of inorganic benzene.
- 13. Why aluminium utensils should not be kept in water overnight.
- **14.** Explain what happens when boric acid is heated.
- 15. BCl₃ exists but BH₃ does not. Explain.
- **16.** Why SnCl₄ is more covalent than SnCl₂?
- **17.** Why PbCl₄ is good oxidising agent?
- **18.** What are germanes and plumbanes?
- 19. Give one example of zeolite.
- 20. Mention the type of hybridization of carbon in diamond and graphite.
- **21.** Why CCl₄ is insoluble in water but SiCl₄ is soluble in water? Explain.
- **22.** Give two uses of silicones.
- 23. Why graphite is used as lubricant?
- **24.** Lead (Pb) do not form PbI₄. Why?
- **25.** CO₂ is gas while SiO₂ is solid at room temperature. Explain why?
- **26.** Explain why silicon shows a higher covalency than carbon?
- 27. Out of carbon and silicon which can form multiple bonds and why?
- 28. Write the formula of dry ice.
- **29.** Mention the basic building unit of all silicates.
- **30.** Graphite is a good conductor of electricity, but diamond is not. Why?
- **31.** Give chemical equation in support of the fact that all bonds in molecule of PCl₅ are not equivalent.

- 32. Why does NH₃ act as a complexing agent?
- **33.** Why is ammonia highly soluble in water?
- **34.** Name the gas evolved when $(NH_4)_2Cr_2O_7$ is heated.
- **35.** Why dinitrogen is much less reactive at room temperature?
- **36.** Why pentahalides are more covalent than trihalides?
- **37.** PCl₅ exist but NCl₅ does not exist. Give reason.
- **38.** NF₃ is not hydrolysed while NCl₃ can be readily hydrolysed. Give reason.
- **39.** What is the basicity of H_3PO_3 ?
- **40.** Why NO₂ dimerises to form N₂O₄?
- **41.** In PCl₅ all five P Cl bonds are not identical. Explain
- 42. NO is a colourless gas but becomes brown on releasing in air. Give reason.
- **43.** What is the covalency of nitrogen in N_2O_5 ?
- **44.** Why is bond angle in PH₄ ion higher than that in PH₃?
- **45.** Arrange in order of increasing bond angle: NO₂, NO₂⁺, NO₂⁻
- **46.** Why PCl₃ fumes in moisture?
- **47.** PCl₅ is ionic in solid state. Why?
- **48.** Why has PH₃ lower boiling point than NH₃?

- 1. Draw the structure of diborane.
- 2. What happens when:
 - (a) Borax is heated strongly.
 - (b) Boric acid is added to water.
- **3.** Write balanced chemical equations for :
 - (a) $BF_3 + LiH \longrightarrow$
 - (b) $B_2H_6 + NH_3 \longrightarrow$
- **4.** Write chemical reactions to justify amphoteric nature of Al.

- 5. Suggest reason why the B-F bond length in BF_3 and BF_4 differ.
- **6.** Give reason for the following:
 - (i) BF₃ act as weak Lewis acid.
 - (ii) Boron cannot show covalency more than four.
- 7. How can you explain higher stability of BCl₃ as compared to TlCl₃?
- **8.** Give reason for the following:
 - (i) Aluminium alloys are used to make aircraft body.
 - (ii) Aluminium wire is used to make transmission cables.
- 9. Describe the shapes of BF₃ and BH₄⁻. Assign the hybridization of boron in these species.
- 10. Explain the chemistry of borax bead test.
- 11. $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ not. Give reason.
- **12.** Hydrolysis of SiCl₄ take place but of CCl₄ does not. Why?
- 13. Account for the following:
 - (a) CO₂ is gas while SiO₂ is solid at room temperature.
 - (b) Solid CO₂ is known as dry ice.
- **14.** Elemental silicon does not form graphite like structure as carbon does. Give reason.
- 15. Suggest a reason as to why CO is poisonous?
- **16.** How is excessive content of CO₂ responsible for global warming?
- 17. What is allotropy? Name two elements which exhibit allotropy.
- **18.** Write equations for the production of water gas and producer gas from coke.
- **19.** Define zeolite. Name the zeolite which converts alcohols directly into gasoline.
- **20.** Arrange the hybrides of group 14 elements in increasing order of :
 - (a) Thermal stability
 - (b) Reducing power.

- 21. What happens when (write chemical equations only)
 - (i) H₃PO₃ is heated.
 - (ii) $(NH_4)_2Cr_2O_7$ is heated
- 22. Complete the reactions:
 - (i) $Cu + HNO_3$ (Cone.) \rightarrow
 - (ii) $I_2 + HNO_3$ (Cone.) \rightarrow
- 23. Draw the structure of N_2O_5 & $H_4P_2O_7$
- **24.** Complete the following reactions:
 - (i) $NH_4Cl(aq) + NaNO_2(aq) \rightarrow$
 - (ii) $P_4 + NaOH + H_2O \rightarrow$
- **25.** State and explain the favourable conditions according to Le Chateleir's Principle for preparation of ammonia by Haber's process. Give reason:
 - (i) NH₃ is basic while PH₃ is feebly basic in nature.
 - (ii) Nitrogen show catenation tendency less than phosphorous.

- 1. Give reasons of the following:
 - (i) In diborane, two B—H—B bonds are different from common covalent bonds.
 - (ii) Aluminium metal shows amphoteric behaviour.
 - (iii) Quartz is used to develop extremely accurate clocks.
- **2.** A certain salt X gives the following results :
 - (i) Its aqueous solution is alkaline to litmus.
 - (ii) It swells up to a glassy material Y on strong heating.
 - (iii) When conc. H_2SO_4 is added to a hot solution of X, white crystal of an acid Z separates out. Write equations for all the above reactions and identify X, Y and Z.
- **3.** Write balanced equation for :
 - (i) $B_2H_6 + H_2O \longrightarrow$
 - (ii) Al + NaOH \longrightarrow
 - (iii) NaOH + $B_2H_6 \longrightarrow$

- **4.** List two important properties in which boron differs from the rest of the members of group. Mention the main reasons for the difference.
- 5. What are electron deficient compounds? Are BCl₃ and SiCl₄ electron deficient species? Explain.
- **6.** Select the member(s) of group 14 that :
 - (i) Forms the most acidic dioxide.
 - (ii) Is commonly found in + 2 oxidation state.
 - (iii) Used as semiconductor.
- 7. What are allotropes? Sketch the structure of two allotropes of carbon namely diamond and graphite.
- **8.** Give suitable reasons for the following:
 - (a) CO₂ turns lime water milky, but if passed for a long time, the solution become transparent again.
 - (b) Graphite is a good conductor of electricity but diamond is insulator.
 - (c) Lead (IV) chloride is highly unstable towards heat.
- 9. (i) Write the resonance structure of CO₃²⁻ and HCO₃⁻.
 - (ii) Write the name of thermodynamically most stable form of carbon.
- **10.** (i) Explain why is there a phenomenal decreases in ionisation enthalpy from carbon to silicon?
 - (ii) Write an industrial application of silicones.
- 11. A compound 'A' on heating gives a brown gas 'B'. The gas 'B' dimerises on cooling to form colourless solid 'C. Identify 'A', 'B' & 'C. Write chemical equations involved.
- 12. Write balanced equations for:
 - (i) $Cu^{2+} + NH_3(1) \rightarrow$
 - (ii) $Ca_3P_2 + HCl \rightarrow$
 - (iii) $Zn + HNO_3$ (Cone.) \rightarrow

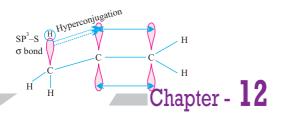
13. Give reason:

- (i) N-N bond dissociation enthalpy is less than P-P bond dissociation enthalpy.
- (ii) $R_3P = O$ exists but $R_3N = O$ does not.
- (iii) CN⁻ ion exists but CP⁻ does not.

- 1. When metal X is treated with NaOH, a white precipitate 'A' is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound 'A' is soluble in dilute HCl to form compound 'C'. The compound 'A' when heated strongly gives 'D', which is used to extract metal. Identify X, A, B, C and D. Write suitable equations to support their identities.
- 2. (i) If B-Cl bond has dipole moment explain why BCl₃ molecules has zero dipole moment.
 - (ii) A mixture of dil. NaOH and aluminium pieces is used to open drain. Give reason.
 - (iii) Aluminium wire is used to make transmission cables. Why?
- **3.** (i) Identify the compounds X and Y in the following reactions:
 - (a) $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + X$
 - (b) $X \xrightarrow{370 \text{ K}} \text{HBO}_2 \xrightarrow{>370 \text{ K}} Y$.
 - (ii) Write the name of group 13 element which is used to measure high temperature.
 - (iii) Why in case of thallium + 1 oxidation state is more stable than + 3?
- **4.** Compare the general trend in the following properties of the elements of group 13 and 14:
 - (a) Atomic size, (b) Ionisation enthalpy, (c) Metallic character,
 - (d) Oxidation states, (e) Nature of halides.

5. Name the following :

- (a) The crystalline form of silica used in modern radio and T.V. broadcasting and mobile radio communication.
- (b) The oxides of carbon which form a complex with haemoglobin 300 times more faster than oxygen.
- (c) The allotrope of carbon which has $\Delta_f H^{\theta} = 0$.
- (d) A type of polymer is semiorganic in nature.
- (e) Two man made silicates.
- **6.** Explain the formation of (i) water gas (ii) producer gas. Give their uses. What happens when CO₂ is passed through limewater? (i) for short duration (ii) for long duration.
- 7. A translucent waxy solid (A) on heating in an inert atmosphere is converted to its allotropic form (B). The solid (A) on reaction with NaOH liberates a gas (C) with rotten fish smell. With excess of chlorine (A) forms (D) which hydrolyses to compound (E). Identify (A) to (E) and write chemical reactions involved.
- 8. Ammonium dichromate on heating gives a gas 'A' which reacts with hydrogen in presence of catalyst to give another pungent smell gas 'B'. Gas 'B' freely dissolves in water to give a weak base 'C Aqueous solution of CuSO₄ reacts with 'C to produce a deep blue colour compound 'D'. Identify A, B, C & D and write chemical reactions involved.



Organic Chemistry: Some Basic Principles And Techniques

- The branch of chemistry which deals with hydrocarbons and their derivatives is called **organic chemistry**.
- Carbon forms large number of organic compound because of its properties of catention and tetravalency.
- **Functional Group :** An atom or a group of atoms, joined in a specific manner, which provides certain characteristics chemical properties to the organic compounds, is called **functional group.**
- **Homologous**: A group or series of an organic compound each containing a characteristics functional group from a homologous series and the members of the series are called **"homologous"**. Each successive member differ by –CH₂ in molecular formula (14 in molar mass).
- Fission of a Covalent Bond :
 - (a) Homolytic cleavage: In this cleavaage, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms.

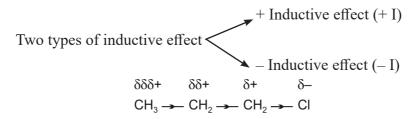
$$Cl \rightarrow Cl + Cl$$
Free Radicals

(b) Heterolytic cleavage: In heterolytic cleavage the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragment.

$$H_3C$$
 $C1 \rightarrow H_3\overset{+}{C} + C1$
Ions

• Electron displacement effects in sigma covalent bonds.

Inductive effect (I): Polarisation of a bond caused by the polarisation of adjacent bond is referred to as the inductive effect.



• It is a permanent effect and decrease with the increase in distance.

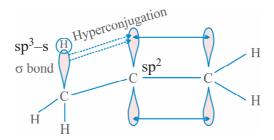
$$- I ext{ effect : } -NO_2 > --F > --Cl > --Br > --I > --OCH_3 > - C_6H_5 \\ + I ext{ effect : } --C(CH_3)_3 > --CH(CH_3)_2 > --C_2H_5 > --CH_3 \\$$

- Electromeric effect: The complete transfer of the shared pair of π electrons of a multiple bond to one of the atoms in the presence of the attacking reagent is called **electromeric effect.**
- If the transference of e^- towards attacking reagent + E effect.
- If the transference of e^- takes place away from attacking reagent E effect.

• Resonance effect (+ R effect): The polarity produced in the molecule by the interaction of two π -bond and lone pair of electrons present on an adjacent atom.

• **Hyperconjugation**: It is special kind of resonance in which delocalisation of e^- takes place through overlap between σ -bond orbital and π -orbital.

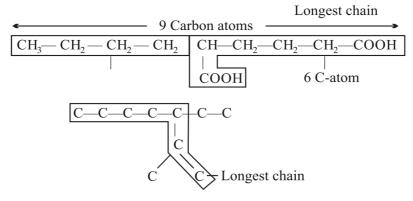
It is also called no bond resonance.



• **IUPAC Nomenclature of Organic Compounds :** Following rules are used to write the IUPAC name of an organic compound.

Rule 1.: Longest chain rule: The chain containing the principal functional group, secondary functional group and multiple bonds as many as possible is the longest possible chain.

In the absence of functional group, secondary group and multiple bonds, the chain containing the maximum number of C-atoms will be the longest possible chain *e.g.*,



Choose the word root from the table given below for the longest possible chain.

Word Root for Carbon Chain

Chain length	Word root	Chain length	Word root
C_1	Meth-	C_7	Hept
C_2	Eth-	C_8	Oct
C_3	Prop-	C_9	Non
C_4	But-	C ₁₀	Dec
C_5	Pent-	C ₁₁	Undec
C_6	Hex-	C ₁₂	Dodec

Rule 2: Lowest number rule: Numbering is done in such a way so that:

- (1) branching if present gets the lowest number.
- (2) the sum of numbers of side chain is lowest.
- (3) principal functional group gets the lowest number.

Select the principal functional group from the preference series:

$$-COOH > -SO_3H > -COOR > -COX > -CONH_2 > -CN > -NC$$

> $-CHO > C = O > -OH > -SH > -NH_2 > -OR > = > =$

Functional group other than the principal functional group are called substituents.

Rule 3

• Naming the prefixes and suffixes: Prefix represents the substituent and suffix is used for principal functional group.

Primary prefixes are cyclo, bicyclo, di, tri, tetra, tetrakis etc.

Secondary prefixes are tabulated below:

Substituent	Prefix	Substituent	ent Prefix	
—F	Fluoro	N=N	diazo	
—C1	Chloro	N=O	nitroso	
—Br	Bromo	$-NO_2$	nitro	

Primary suffix are **ene**, **ane** or **yne** used for double, single and triple bonds respectively.

Secondary suffixes are tabulated below:

S.No.	Class	Formula	Prefix	Suffix
		О		
1.	Acid halides	—C—X	halocarbonyl	—oyl halide
2.	Alcohols	—ОН	hydroxy	—ol
3.	Aldehydes	—СНО	formyl	—al
			—carbaldehyde	
4.	Ketones	C = O	oxo (keto)	—one
5.	Amides	—CONH ₂	carbamoyl	—amide

6.	Amine	NH_2	amino	—amine
7.	Carboxylic acid	—СООН	carboxy	—carboxylic acid
8.	Ester	—COOR	alkoxy carbonyl	—alkyl alkan oate
9.	Nitriles	—CN	cyano	—nitrile
10.	Sulphonic acid	—SO ₂ —OH	sulpho	—sulphonic acid

Here according to the rules, given above, the IUPAC name of a compound can be written as \Rightarrow Prefixes + Word root + Suffixes.

 Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

for e.g.,
$$CH_3$$
 $CH - CH_2$ CHO \leftarrow Principal functional group

(—al)

OH — substituent (hydroxy)

3 — Hydroxybutanal

↑ ↑ ↑

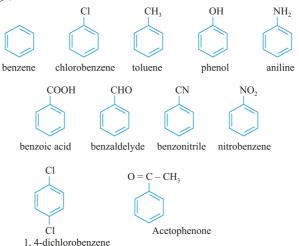
prefix word suffix

root

• If more than two similar functional groups are present, all the groups are considered as substituent, for *e.g.*,

Propane-1, 2, 3-tricarbonitrile

• Naming of Aromatic compounds: IUPAC accepted their common trivial names *e.g.*,



• Purification and Characterization of Organic Compounds :

(1) Lassaigne's test for nitrogen: Lassiagne's extract is heated with FeSO₄ solution in presence of alkali, the solution is cooled and acidified with dil. H₂SO₄. If a green or blue colouration is obtained, it confirms the presence of N in the organic compound. The chemistry of the test is:

$$Na + C + N \longrightarrow NaCN$$

From organic compound

$$2\text{NaCN} + \text{FeSO}_4 \rightarrow \text{Fe[CN]}_2 + \text{Na}_2\text{SO}_4; \text{Fe[CN]}_2 + 4\text{NaCN} \rightarrow \text{Na}_4[\text{Fe(CN)}_6]$$
 Sodium ferrocyanide

$$3\text{Na}_4[\text{Fe(CN)}_6] + 4\text{Fe}^{3+} \xrightarrow{x\text{H}_2\text{O}} \text{Fe}_4[\text{Fe(CN)}_6]_3.x\text{H}_2\text{O} + 12\text{Na}^+$$
Ferric ferrocyanide (Prussian Blue)

This test is very delicate and is given by all compounds containing C and N. Hydrazine do not respond to this test since they do not contain carbon.

Formation of blood red colour indicates the presence of both N and S.

$$Na + C + N + S$$
 $\xrightarrow{\Delta}$ $NaSCN$

From organic compound Sodium thiocyanate or Sodium sulphocyanide

$$Fe^{3+} + Na SCN \rightarrow [Fe(SCN)]^{2+} + Na^{+}$$

Ferric thiocyanate (blood red colour)

- **Detection of sulphur :** If S is present, during fusion with Na metal, Na₂S is formed which may be tested as follows :
 - (i) With sodium nitroprusside violet colouration is produced :

$$Na_2S + Na_2[Fe(CN)_5(NO)] \rightarrow Na_4[Fe(CN)_5(NOS)]$$

Sodium nitroprusside (Violet colour)

(ii) With lead acetate, black precipitate of PbS is formed.

$$Na_2S + (CH_3COO)_2 Pb \rightarrow PbS + 2CH_3COONa$$

- Detection of halogens :
 - (a) Lassaigne's test: When the organic compounds is fused with Na metal, the halogens combine with Na to form sodium halides.

The presence of these halides is tested with AgNO₃ solution.

- (i) A white ppt. soluble in NH₄OH indictes chlorine.
- (ii) A pale yellow ppt. partially soluble in ammonia indicates bromine.

(iii) A yellow ppt. insoluble in ammonia indicates iodine.

If the organic compound also contain N or S, the sodium extract is first boiled with dil. HNO₃ to decompose any cyanides or sulphides, otherwise these will form ppt. with AgNO₃ solution.

- **Detection of phosphorus:** Phosphorus is detected by fusing the organic compound with sodium peroxide, in which phosphorus is converted into sodium phosphate.
 - The fused mass is extracted with H₂O and then boiled with conc. HNO₃ and then ammonium molybdate is added. Appearance of yellow ppt. or yellow colouration due to the formation of ammonium phosphomolybdate indicates the presence of phosphorus.
- Estimation of carbon and hydrogen: Liebig's method: A known mass of the organic compound is heated strongly with excess of dry copper oxide in a current of dry air or oxygen (free from CO₂) when carbon present in the organic compound is oxidised to CO₂ and hydrogen to H₂O.

$$C + 2CuO \xrightarrow{\Delta} CO_2 + 2Cu; 2H + CuO \xrightarrow{\Delta} H_2O + Cu$$

Percentage of carbon =
$$\frac{12}{44} \times \frac{\text{Mass of CO}_2 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

Percentage of Hydrogen =
$$\frac{2}{18} \times \frac{\text{Mass of H}_2\text{O formed}}{\text{Mass of substance taken}} \times 100$$

- **Estimation of nitrogen:**
 - (a) Dumas method:

 $N + CuO \longrightarrow N_2 + Small$ amounts of oxides of nitrogen

Oxides of nitrogen + Cu
$$\stackrel{\Delta}{\longrightarrow}$$
 CuO + N₂

Percentage of nitrogen =
$$\frac{28}{22400} \times \frac{\text{Vol. of N}_2(\text{in cm}^3) \text{ at STP}}{\text{Mass of substance taken}} \times 100$$

(b) Kjeldahl's method:

Organic compound +
$$H_2SO_4 \xrightarrow{\Delta} (NH_4)_2SO_4 \xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

Percentage of nitrogen:

 $= \frac{1.4 \times Molarity \ of \ the \ acid \times V \ ol. \ of \ acid used \times B \ asicity \ of \ the \ acid}{Mass \ of \ substance \ taken}$

• Estimation of halogens: (Carius method):

$$\textbf{Percentage of chlorine} = \frac{35.5}{143.5} \times \frac{Mass\ of\ AgCl\ formed}{Mass\ of\ substance\ taken} \times 100$$

Percentage of bromine =
$$\frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of substance taken}} \times 100$$

Percentage of iodine =
$$\frac{127}{235} \times \frac{\text{Mass of AgI formed}}{\text{Mass of substance taken}} \times 100$$

• **Percentage of sulphur** =
$$\frac{32}{233} \times \frac{\text{Mass of BaSO}_4 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

• Estimation of phosphorus: A known mass of the organic compound is heated with fuming HNO₃ in a Carius tube when phosphorus of the organic compound is oxidized to H₃PO₄. Phosphoric acid thus formed is precipitated as magnesium ammonium phosphate by adding magnesia mixture (a solution containing MgCl₂, NH₄Cl and NH₄OH.)

Percentage of phosphorus :
$$\frac{62}{222} \times \frac{\text{Mass of Mg}_2\text{P}_2\text{O}_7 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

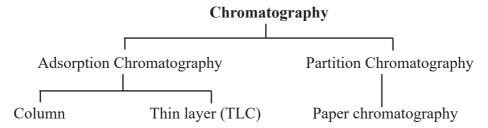
Estimation of oxygen: A definite mass of an organic compound is decomposed by heating with N₂ gas. The mixture is then passed over red hot coke when all oxygen is converted to CO. This mixture is then passed through I₂O₅ when CO is oxidised to CO₂ producing iodine. The % of oxygen can be derived from the amount of CO₂ or I₂ produced.

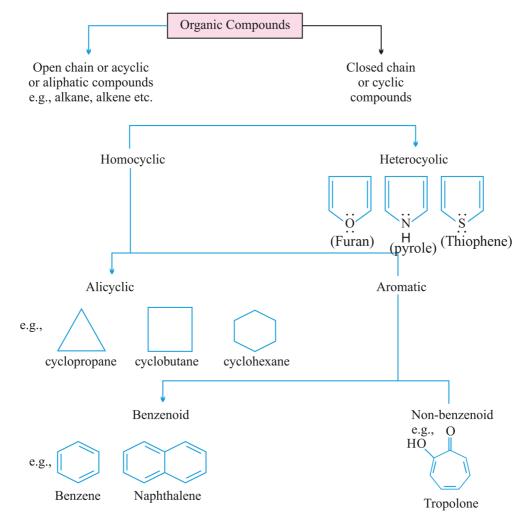
Percentage of oxygen :
$$\frac{16}{44} \times \frac{\text{Mass of CO}_2 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

Method of Purification of organic compounds:

• **Crystallisation:** Process of solidification of a pure substance from its dissolved state. This method is based upon differences in their solubility in a given solvent or in mixture of solvents.

- **Sublimation :** It is a process of conversion of a solid into gaseous state on heating without interchanging into liquid. The process is used for the separation of volatile solids, which sublime on heating from the non-volatile solids.
- **Distillation**: It is a process of conversion of a liquid into vapours by heating followed by condensation of vapours. The method is used for the purification of liquids which boil without decomposition and are present with non-volatile impurities.
- Fractional distillation: Process used to separate mixture of two or more miscible liquids having different boiling points. It is mainly used in distillation of petroleum, coaltar and crude oil.
- **Distillation under reduced pressure :** This process is used when the liquid has a tendency to decompose near its boiling point. Under reduced pressure, the liquid will boil at a low temperature without decomposing.
- **Steam distillation:** Purification of a substance from non-volatile impurities provided the substance itself is volatile in steam and insoluble in water.
- Chromatography: Technique of separating the consitituents of a
 mixture by the differential movement of individual components through
 the stationary phase under the influence of mobile phase. Two types of
 chromatography.





- 1. Identify the most electronegative element in CH₂FCl.
- 2. Write the hybrid orbitals used by 'C' in ethene.
- 3. Identify the tertiary (3°) and quarternary (4°) carbon in CH₃
- 4. How many σ and π bonds are there in given organic compound.

6. How many σ and π bonds are present in each of the following molecules?

(a)
$$HC = CCH = CHCH_3$$
 (b) $CH_2 = C = CH - CH_2CH_3$ [Ans. (a) $\sigma = 10$, $\pi = 3$ (b) $\sigma = 12$, $\pi = 2$]

7. Mention the hybridisation of C* and shape of the compound.

(a)
$$H_2C^* = O$$
 (b) $CH_3 - C^* = N$

8. Which bond in more polar in the following pair of molecules:

- 9. Draw formula of first four members of homologeous series begining with the compound $CH_2 = CH_2$.
- 10. (a) Why does carbon exhibit catenation to maximum extent?
 - (b) Give hybridization of each carbon in following compound CH₂=CH—CN.

Nomenclature

1 - Mark Questions

1. Write the IUPAC name of

(a)
$$CH_3$$

(b) CH_3 — C — $CH = CH$ — CH_2 — $COOH$
 CH_3

- 2. Draw structure of 3-isopropyl-2-methylhexane.
- 3. Write the structure of compound that contains both 1° and 2° alcohol.
- **4.** Give IUPAC name of following :

5. Give IUPAC name of following bond-line formulae:



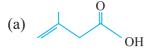
2 - Mark Questions

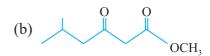
6. Write the correct order of priority of the following functional groups :

$$\begin{matrix} \text{O} & \text{O} \\ \parallel & \parallel \\ -\text{C} = \text{N}, -\text{C} -, -\text{OH}, -\text{C} - \text{OH} \end{matrix}$$

- 7. Write the structural formula of:
 - (i) o-Ethylanisole

- (b) 4-Ethyl-1-fluoro-2-nitrobenzene
- 8. Identify the functional groups in:





9. Give IUPAC name of following:

(a)
$$CH_3 - (CH_2)_3 - CH - CH (CH_3) - CH (CH_3)_2$$

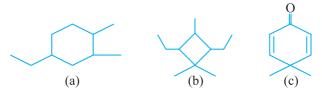
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$$CH_2 - CH_2 - CH (CH_3)_2$$



- **10.** Give condensed and bond-line structural formulae and identify the functional group(s) present, if any for :
 - (a) Cycloocta-1, 5-dine
 - (b) 2(4-isobutylphenyl) propanoic acid

- 11. Draw the structure of:
 - (a) Pent-3-enoic acid
 - (b) 4-Methylpentanone
 - (c) 4-Ethyl-3-fluorophenol.
- 12. Write the IUPAC name of the following compound:



Isomerism

1 - Mark Questions

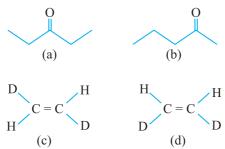
- 1. Write functional isomer of molecular formula C₃H₆O.
- 2. Write tautomeric form of following structures:



3. Identify the chiral carbon in the given compound

2 - Mark Questions

4. What is the relationship between the members of the following pairs of structures?



5. Write all the possible isomers of the aromatic compound C₈H₁₀.

Concepts in Reaction Mechanism

- 1. Identify electrophilic centre in CH₃CHO.
- 2. Identify nucleophilic centre in CH₃Br.

3. Arrange the following in decreasing order of stability:

$$\dot{\mathrm{CH}}_3, (\mathrm{CH}_3)_2 \dot{\mathrm{C}} - \mathrm{CH}_2 \mathrm{CH}_3, \mathrm{CH}_3 - \mathrm{CH}_2 - \mathrm{CH}_2$$

4. Which of the following species can act as an acid and why?

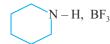
- **5.** What types of attacking reagents are produced by heterolytic cleavage of bonds?
- **6.** Out of CH₃COOH and NO₂CH₂COOH which is more acidic in nature and why?
- 7. Identify the most stable carbocation among the following:

$$H_2C = \overset{+}{C}H, CH_3 - CH = \overset{+}{C}H, \overset{+}{C}H_3$$

8. Identify the weakest nucleophile among the following:

$$\bar{N}H_2$$
,CH₃ — \bar{N} — CH₃,CH₃ — $\bar{N}H$

9. Select the nucleophile and electrophile in the following:



10. Give reason $(CH_3)_3C^+$ is more stable than $CH_3\overset{+}{C}H_3$ and $\overset{+}{C}H_3$.

2 - Mark Questions

11. Mark the electrophillic centre in the following molecules:

- **12.** Benzylic free radical is more stable than allylic free radical. Explain with resonance.
- **13.** Classify each of the following carbon intermediates :

(a)
$$(CH_3)_3C^+$$

(b)
$$CH_3 - \overset{\ominus}{CH} - CH_3$$

14. Classify whether the following reaction is rearrangement addition, or elimination?

$$CH_3-CH = CH_2 + HBr \longrightarrow CH_3-CH-CH_3$$

15. Write the product of following reaction.

(1)
$$H_3C-\equiv C-CH_3 \xrightarrow{Na} \frac{Na}{liq NH_3}$$

(2)
$$CH_3CH_2CH_2CH_3 \xrightarrow{AlCl_3} \xrightarrow{Heat}$$

- **16.** Write structure of various carbocation that can be obtained from 2-methylbutane. Arrange thee carbocation in order of increasing stability.
- 17. Classify the reaction type as elimination, rearrangement addition and substitution.

(a)
$$CH_2CH_2OH$$
 $CH = CH_2$ $+ Conc. H_2SO_4$ \longrightarrow OH OH (b) CH_3 — $CH(Br)$ — $CH(CH_3)_2$ $\xrightarrow{aq. KOH}$ CH_3CH_2 — C — $CH(CH_3)_2$

18. Follow the flow of electrons indicated by the curved arrows and predict the products :

(a)
$$O \longrightarrow H$$
 \cdots $CH_3 \longrightarrow CH_3 \longrightarrow CH_3 + :OH$ CH_3

(c)
$$CH_3 - C \longrightarrow C \longrightarrow H$$
 H
 H

- 19. Name the electrophile/nucleophile generated by following species :
 - (a) $HNO_3 + H_2SO_4$
 - (b) CH₃COCl
 - (c) alc. KCN

20. Identify the nucleophiles, electrophiles and free radicals amongst the following:

- 21. Which is more stable and why? (a) $C_6H_5CH_2$ or $C_6H_{11}CH_2$ (b) $(C_6H_5)_2$ $\dot{C}H$ or $C_6H_5\dot{C}H_2$

 - (c) $C_6H_5\dot{C}H_2$ or $CH_2=CH-\dot{C}H_2$

5 Mark Questions

(a) Arrange the following according to given property:

$$CH_3CH_2$$
, $C_6H_5CH_2$, $(CH_3)_3C^+$, $CH_2=CHCH_2$
(dereasing order of stablity)

- (b) $HC \equiv C, CH_2 = CH, CH_3 CH_2, CH_3$ (increasing order of stability)
- (c) $C_6H_5\dot{C}HCH_3$, $C_6H_5CH_2\dot{C}H_2$, $C_6H_5\dot{C}(CH_3)_2$ (increasing order of stability)

(d)
$$CH_3CH$$
— CH_3 , CH_3 — CH — OCH_3 , CH_3CH — C — OCH_3

(dereasing order of stablity)

(e) $(CH_3)_3 \stackrel{\overline{..}}{C}, (CH_3)_2 \stackrel{\overline{..}}{C}H, CH_3 \stackrel{\overline{..}}{C}H_2$ (decreasing order of stablity)

Electronic Displacement in Covalent Bond

- 1. Name the kind of effect that operates to explain the stability of carbocations.
- 2. Why inductive effect is also called transmission effect?
- 3. Which permanent effect of organic compound is also known as 'No bond resonance effect'?
- 4. Which is correct and why?

$$C = C + E^{+}$$
 Or $C = C + E^{+}$

- **5.** Write resonating structure of the following and show the movement of electron by curved arrows :
 - (a) CH₃—COO-

(b)
$$CH_2 = CH - C1$$

- **6.** Draw the resonating structure of :
 - (a) $N = N \frac{1}{N} H$

- 7. Write resonance structure of:
 - (a) $C_6H_5NH_2$

- (b) $C_6H_5NO_2$
- 8. Explain why alkyl groups acts as e^- donar when attached to a π -system.
- **9.** Resonance structures of propenal are given below. Which of these resonating structure is more stable? Give reason.

$$CH_2 = CH$$
— $CH = O \longleftrightarrow CH_2$ — $CH = CH$ — \bar{O}
(I)
(II)

- 10. Explain the following terms:
 - (a) Electromeric effect
- (b) Hyperconjugation
- 11. (a) Explain + I and I effect.
 - (b) Select the group giving + I effect and I effect from the following list:
 - (i) $-NO_2$ (ii) -CN (iii) Cl^- (d) CH_3^-
- **12.** Explain the importance of inductive effect in determination of acidic or basic strength of substances.

- (a) Give reason for the following:
 - (a) Chlorobenzene is O⁻ and P⁻ directing towards the electrophillic substitution reaction.
 - (b) Inductive effect decrease with the increase in distance.
 - (c) Hyperconjugation effect is extended form of resonance effect.
- **(b)** Arrange the following according to given property:
 - (a) — NO_2 , —COOH, —F, —CN, —I (increasing order of I effect)
 - (b) CH₃—, (CH₃)₂C—, (CH₃)₂CH—, CH₃CH₂— (decreasing order of + I effect)

- 1. What conditions must be satisfied by a suitable solvent in the crystallization method?
- 2. Which technique can be used for purification of iodine that contains traces of NaCl?
- 3. When do we use hot water funnel for filteration?

[Hint: When organic substance crystallises during filtration.]

- **4.** A liquid (10 mL) has three components A, B, C. Which technique is most suitable to separate A, B, C from such a small amount of mixture?
- 5. A substance has boiling point 355 K, but it starts decomposing near this temp. Which type of distillation process is suitable for its purification?
- **6.** Name the adsorbent used in column chromatography.
- 7. Which technique can be used to separate naphthene from kerosene oil present in its mixture?
- **8.** A mixture contains nitrobenzene and benzoic acid. How can this mixture be separated into its constituents by technique of extraction using appropriate chemical reagent?

[Hint: By using hot water as solvent and adopting differential extraction.]

- 9. Name a suitable technique of separation of the components from a mixture of:
 - (a) Water and aniline.
 - (b) Methanol and Propanone.

2-Mark Questions

- 1. A student was given the compound C₆H₄(NH₂)SO₃H for elemental analysis, while performing Lassaigne's test for N, what colour will he get and why?
- 2. Why diazonium salts do not show sodalime test for nitrogen?

[Hint: Because salts do not liberate NH₃ gas under there conditions.]

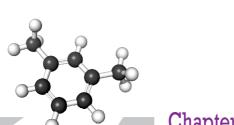
- **3.** What is the function of fusing the organic compound with sodium metal?
- **4.** If silver nitrate solution is added to chlorobenzene, will there be formation of white ppt.
- 5. Name the oxidising agent used in the combustion tube along with the organic compound. [Ans. CuO]
- 6. Why is it necessary to boil Lassaigne's extract with HNO₃ before testing it for halogens?
- 7. 0.25 g of an organic compound containing C, H and O was analysed by the combustion method. The increase in the mass of calcium chloride tube and the potash bulbs at the end of the operation was found to be 0.15 g and 0.1837 g respectively. Calculate the percentage composition of the compound.
- **8.** Will CCl₄ give white precipitate of AgCl on heating it will silver nitrate? Give reason.
- 9. For which type of compounds Kjeldahl's method is not applicable?
- 10. 0.90 of an organic compound on combustion 2.64 g of CO₂ and 0.63 g of H₂O. Calculate the percentage of C and H in the compound.

- 11. What will happens if a student acidifies the Lassaigne's extract with dil. H₂SO₄ in place of dilute HNO₃. Write the reaction involved.
- 12. (a) In DNA and RNA, nitrogen atom is present in the ring system. Can Kjeldahl's method is used for the estimation of N-present in these. Give reasons.
 - (b) Why is it necessary to use ethanoic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?
- 13. 0.2325 g of an organic compound was analysed for nitrogen by Duma's method. 0.0317 L of moist nitrogen was collected at 25°C and 755.8 mm pressure calculate the percentate of nitrogen. Aq. tension of water at 25°C is 23.8 mm Hg.

5-Mark Questions

14. (a) Out of the different gases formed in Duma's method, which gas is not observed over an aqueous solution of KOH.

- (b) What is the function of adding small amount of K_2SO_4 and a little amount of Hg or $CuSO_4$ is Kjeldahl's flask?
- (c) Explain why a solution of KOH used to absorb CO₂ evolved during the estimation of carbon in an organic compound.
- (d) An organic compound contain diazo group (—N=N—) or nitro group or 'N' in the ring. Name the method used to estimate nitrogen in the compound.
- 15. (a) 0.4 g of the compound was Kjeldahl's and ammonia evolved was absorbed into 50 ml of $\frac{M}{4}$ H₂SO₄ solution. The residual acid solution was diluted with distilled water and the volume was made upto 150 ml. 20 ml of this diluted solution required 31 ml of $\frac{M}{20}$ NaOH solution for complete neutralization. Calculate the % of N is compound.[Ans.46.8%]
 - (b) Write the formula for the pursian blue colour obtained during Lassaigne's test for nitrogen.
 - (c) Give test to detect the presence of sulphur in compound.



Chapter - 13

Hydrocarbons

• Preparation of Alkanes:

(1) From unsaturated hydrocarbons:

(2) Wurtz reaction $\begin{bmatrix} Alkyl \ Halide + Na & Dry \\ ether \end{bmatrix}$ Higher alkane

$$R-X + 2Na + X-R$$
 Dry ether $R-R + 2NaX$

(3) Decarboxylation:

[Sodium salt of carboxylic acid + NaOH + CaO \rightarrow Alkane [$n_c = 1$ less]

$$R - CH_{2} \xrightarrow{O} C - O Na^{+} + NaOH \xrightarrow{CaO} R - CH_{3} + Na_{2}CO_{3}$$
Alkane

(4) Kolbe's Electrolysis:

 $\left[\text{Potassium salt of carboxylic acid (aq)} \xrightarrow{\quad \text{Current} \quad} \text{Higher alkane} \right]$

$$R-CH_2 \stackrel{\searrow}{\xrightarrow{}} C - O K^+$$

• Chemical Properties of Alkanes:

(1) Halogenation: One (H) atom is replaced by halogen at a time.

$$CH_4(g) + Cl_2(g) \xrightarrow{hv} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$$

(2) **Aromatization**:
$$n$$
-Hexane $\xrightarrow{\text{Cr}_2\text{O}_3 \text{ or V}_2\text{O}_5}$ or or

Preparation of alkenes :

(1) From alkynes [Alkyne + $H_2 \longrightarrow Alkene$]

$$R-C \equiv C-R$$

$$R = C = C$$

$$R$$

$$H$$

$$C = C$$

$$H$$

$$R$$

trans alkene

(2) From alkyl halide by (dehydrohalognation)

Alkyl Halides + alc.KOH
$$\stackrel{\Delta}{\longrightarrow}$$
 Alkene

Carbon attached with halogen is α -carbons

Carbon attached with α -carbons is β -carbons

Halogen is removed and 'H'-atom is removed from β -carbon to form (C = C) double bond.

(3) By dehydration of alcohols (Loss of water molecule)

Carbon attached to alcohoic group is α -carbon.

Carbon attached to α -carbon is β -carbon.

(4) From vicinal dihalides [Compounds in which halogen atom are attached with adjacent carbons]

• Chemical Properties of Alkenes :

(1) Addition of Halogens : $\begin{bmatrix} Alkene + X_2 \longrightarrow Vicinal \ dihalide \end{bmatrix}$

$$-C = C - + X_2 \xrightarrow{CCl_4} - C - C - or - C - C - C$$

$$| | or Br_2(1)$$

$$| | or | | | | | | |$$

- (2) Addition of H—X : $\begin{bmatrix} Alkene + HX \longrightarrow Alkyl \ halide \end{bmatrix}$
- (A) **Markownikov's rule (M.R.)**: During electrophillic addition of hydrogen halide, the electron deficient electrophile (E⁺) always attack

on that doubly/triply bounded carbon atom. which already has greater number of hydrogen atoms.

$$CH_{3}-CH = CH_{2} + H \xrightarrow{\wedge} Br \xrightarrow{M.R.} CH_{3}-CH-CH_{2}$$

$$Br \xrightarrow{H} Br \xrightarrow{H}$$

(B) **Peroxide/Kharasch effect (Anti M.Rule)**: This effect takes place in presence of organic peroxides when the hydrogen free radical (H) attacks on that doubly bonded carbon which has lesser number of hydrogen atoms.

$$CH_{3} - CH = CH_{2} + H \xrightarrow{\text{Peroxide}} CH_{3} - CH - CH_{2} + CH_{3}COOH$$

$$\dot{H} \quad \dot{Br} \quad CH_{3} - CH - CH_{2} + CH_{3}COOH$$

(3) Ozonolysis

$$C = C + O_3 \xrightarrow{Zn/H_2O} C = O + O = C$$

In this reaction all those carbons which form double bonds get finally converted into carbonyl carbons. If alkenes are symmetrical then both carbonyl compounds are same.

If more than two double bonds are present then we get atleast one compound which has two carbonyl groups at the end. Such bifunctional compounds are formed from that part of alkene which is in between the double bonds.

$$- \overset{1}{C} = \overset{2}{C} - \overset{3}{C} = \overset{4}{C} - \overset{5}{C} - \overset{2}{C} - \overset{5}{C} - \overset{2}{C} - \overset{2}{C} - \overset{3}{C} - \overset{4}{C} - \overset{5}{C} - \overset$$

For cyclic alkenes:

(D) With potassium paramagnate:

(i) Cold dilute alkaline KMnO₄ = Bayer's reagent.

(1) Cold dilute alkaline Kivino₄ Bayer's reagent.

OH OH

$$-C - C = C - C - + \text{cold dil Alk. KMno}_4 \rightarrow -C - C - C - C$$

[Alkene + cold dil. $KMnO_4 \rightarrow Diol$]

Bayer's test for the presence of (C = C) bond Compound + cold dil. alk. $KMnO_4 \longrightarrow Purple$ colour decolourised \therefore Compound is alkene.

(ii) Hot KMnO₄

$$\begin{array}{c} \text{CH}_{3} & \text{O} \\ \\ \text{CH}_{3} - \text{C} = \text{CH} - \text{CH}_{3} + \text{Hot KMnO}_{4} \xrightarrow{100^{\circ}\text{C}} \text{CH}_{3} - \text{C} - \text{CH}_{3} \\ \\ \text{Ketone} \\ \\ + \begin{array}{c} \text{CH}_{3} - \text{COOH} \\ \text{Carboxylic acid} \end{array}$$

Alkynes

• Preparation:

(1)
$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + HC \equiv CH$$

Calcium carbide Acetylene

(2) From vicinal dihalides $\left[\text{Vicinal dihalide} + \frac{\text{(i) alc. KOH}}{\text{(ii) Na/NH}_3} \longrightarrow \text{Alkyne} \right]$

$$\begin{array}{c|c}
H & H \\
-C - C - C \\
\downarrow & \downarrow \\
X & X
\end{array}
\xrightarrow{alc. KOH}$$

$$\begin{array}{c}
H \\
\downarrow \\
C = C \\
\downarrow \\
X
\end{array}
\xrightarrow{NaNH_2} - C \equiv C - \underbrace{\begin{array}{c}
NaNH_2 \\
or \\
Na in NH_3(1)
\end{array}}$$

$$C \equiv C - \underbrace{\begin{array}{c}
NaNH_2 \\
or \\
Na in NH_3(1)
\end{array}}$$

• Chemical properties:

(1) Hydration [Addition of water]

$$\left[\text{Alkyne} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{Carbonyl compound} \right]$$

$$R - C \equiv C - H + H_2O \xrightarrow{\text{dil } H_2SO_4} \begin{array}{c} O \xrightarrow{\frac{1}{2}} H \longrightarrow O \\ H \xrightarrow{\text{gSO}_4} \end{array} \begin{array}{c} R - C = C - H \\ H \xrightarrow{\text{gSO}_4} \end{array} \begin{array}{c} R - C = C - H \\ H \xrightarrow{\text{gSO}_4} \end{array} \begin{array}{c} O \xrightarrow{\text{grad}} H \longrightarrow R - C - CH_3 \\ H \xrightarrow{\text{gSO}_4} H \longrightarrow R - C - CH_3 \end{array}$$

(2) Addition of Halogen molecule : [Alkyne + $2X_2 \longrightarrow$ Tetrahalides]

(3) **Ozonolysis**: [Alkyne +O₃ → Dicarbonyl compound]

$$-C \equiv C - +O_3 \xrightarrow{Zn} -C -C -$$

(4) Cyclic Polymerisation:
$$3HC \equiv CH \xrightarrow{\text{Fe red hot}}$$

Benzene

• Preparation:

$$(1) \qquad \bigcup_{\parallel} C - ONa^{+} + NaOH \longrightarrow CaO$$

(2)
$$3HC = CH \xrightarrow{\text{Fe red hot tube}} 873K$$

$$(3) \begin{array}{c} O - H \\ + Zn \\ Dust \end{array} \longrightarrow \begin{array}{c} \Delta \\ + ZnO \end{array}$$

Chemical properties of benzene

$$+ \text{Reagent} \longrightarrow + H^{+}$$

(1) Nitration:

$$+ \frac{\text{conc. HNO}_3 + \text{conc. H}_2\text{SO}_4}{\text{NO}_2^+}$$
Nitrobenzene

(2) Halogenation:

$$+ Cl_2/Br_2$$
 Fe Or Br

Chlorobenzene Bromobenzene

(3) Friedal-Craft Alkylation:

$$\begin{array}{c|c} + R - X \\ \text{Alkyl halide} \\ (R^{+}) \end{array} \xrightarrow{\text{Anhydrous}} + HX$$

(4) Friedal-Craft Acylation:

$$\begin{array}{c|c}
O \\
C \\
C \\
C \\
R
\end{array}$$
+ RCOCl or $R - C - Cl$

$$\begin{array}{c}
O \\
Anhydrous \\
AlCl_3
\end{array}$$
+ HCl
$$\begin{array}{c}
O \\
C \\
C \\
C \\
R
\end{array}$$

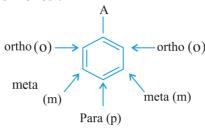
Huckel's Rule:

Conditions: (i) Compound must be cyclic & planar

(ii) Complete delocalisation of πe^-

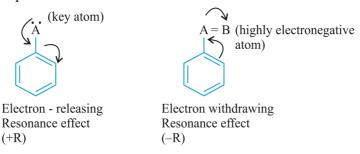
(iii) Presence of $(4n + 2) \pi e^{-}$. (n = 1, 2, 3, ...)

Derivatives of Benzenes:



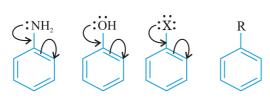
Ortho/Para directors: Group which direct the incoming electrophile to attach at ortho/para positions.

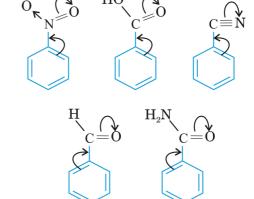
Meta directors: Groups which direct the incoming electrophile to attack at meta position.



Ortho/Para dircetions

Meta directions

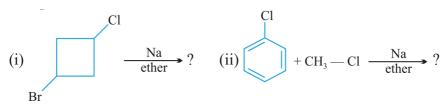




1-Mark Questions

- 1. Give IUPAC name of $CH (CH_3) (CH_2)_4 CH_3$
- **2.** Give the IUPAC name of
- 3. Give the standard formula of 5-sec-butyl, 4-isopropyldecane.
- **4.** Give the standard formula of 4-tert-butyl 4-ethyl-2, 2, 5, 5-tetramethyl hexane.
- **5.** How we can obtain isobutane from *n*-butane?
- 6. *n*-Hexane $\frac{773K, 10-20 \text{ atm}}{V_2O_5}$?

- 7. Out of 2-methylpentane and 2, 3-dimethylpentane which has greater boiling point and Why?
- 8. Give the structure of alkyl halide which when treated with sodium metal in presence of ether gives $(CH_3)_2CH.CH(CH_3)_2$.
- 9. Complete:



- 10. Explain:
 - (i) Staggered form of ethane is more stable than eclipsed form.
 - (ii)Wurtz reaction is carried out in dry ether.

Alkenes

1-Mark Questions

11. Give IUPAC name of



13. Name the effect which decide the stability of alkenes.

14. Complete the reaction : CH_3 — $CH=CH_2 + HBr \frac{Organic}{Peroxide}$?

15. What is product formed during addition of HBr in alkenes in presence of peroxides?

2-Mark Questions

17. Arrange the alkenes in decreasing order of stability. CH₃—CH = CH(CH₃), CH₂ = CH₂, CH₃—CH = CH₂

- 18. Complete the reaction $CH_2 = CH C = CH_2 + O_3 \xrightarrow{ZH_3COOH}$?

 CH₂
- **19.** Complete the reaction:

20. $\left\langle \right\rangle \rightarrow \left\langle \right\rangle + O_3 \xrightarrow{CH_3COOH} ?$

- 21. Name the alkene which will yield a mixture of cyclopentanone and propanal on treatment with O₃ followed by reduction with Zn.
- 22. An alkene on treatment with H—Br in presence of peroxide can generate

23. Explain:

(i) Melting point of *cis-2*-butene is lower than that of trans-2-butene.

(ii) Kharasch/peroxide effect is spontaneous with HBr only.

3 Mark Questions

- **24.** Complete the reactions :
 - (i) $(CH_3)_2C = CH CH_3 + Hot KMnO_4 \longrightarrow$
 - (ii) $(CH_3)_2C = CH.CH_3 + Cold dil. KMnO_4 \longrightarrow$
 - (iii) $(CH_3)_2C = CH.CH_3 + HBr \xrightarrow{Organic Peroxide}$
- **25.** Indicate the reagents used to form the following products :
 - $(i) \longrightarrow OH \qquad (ii) \longrightarrow CHO$ CHO
 - (iii) CH₃ CH₃
- **26.** (i) Convert: iso-propylbromide \longrightarrow *n*-propyl bromide.
 - (ii) Give IUPAC name of Vinyl chloride.

Alkynes

1 Mark Questions

- 27. Give IUPAC name of acetylene.
- **28.** Which alkyne would you start with to prepare CH_3 — CH_2 — CH_2 —CO— CH_3 ?
- **29.** Name the reagent used in the following changes:

$$CH_{3}$$
— $(CH_{2})_{3}$ $C \equiv C$ — $(CH_{2})_{3}$ — CH_{3} $\xrightarrow{?}$ CH_{3} — $(CH_{2})_{3}$ $C = C$
 H
 H

30. Give the alkyne which produce acetic acid and proponoic acid on treatment with alkaline $KMnO_4$ at 100°C.

- **31.** Convert : Acetylene \rightarrow Propylene.
- **32.** Convert : Ethylene \rightarrow Acetylene.
- 33. How you will obtain : $C \equiv C CH_3$ from $C \equiv CH$
- **34.** Give the product when 1-methylcyclohexene reacts with:
 - (i) Aq. acidic $\mathrm{KMnO_4}$ (ii) $\mathrm{O_3}$ followed by $\mathrm{Zn/CH_3COOH.}$

3 Mark Questions

35. Pent-1-yne
$$\xrightarrow{\text{(i) NaNH}_2/\text{NH}_3}$$
 (A) $\xrightarrow{\text{H}_2}$ (B) $\xrightarrow{\text{Br}_2}$ (C) Catalyst

Identity A, B and C compounds and give their reactions.

Benzene

1 Mark Questions

- **36.** Who discovered benzene?
- **37.** Give reason whether is aromatic or not.
- 38. Is pyrrole N an aromatic compound or not? Give reason.

39.
$$+ CH_3COC1 \xrightarrow{Anhy. AlCl_3}$$
?

40. Give major product only CH₃(o/p)

$$NO_2(m)$$
 + conc. HNO_3 + conc. $H_2SO_4 \longrightarrow ?$

41. Give major product only

$$\begin{array}{c}
\text{CH}_{3}(\text{o/p}) \\
+ \text{Br}_{2} \xrightarrow{\text{FeBr}_{3}} ?
\end{array}$$

HOOC

2 Mark Questions

42. (i) Convert Acetylene → Benzene

(ii)
$$+ \text{Cl}_2 \xrightarrow{\text{U.V.}} ?$$

- **43.** Distinguish chemically butyne and but-2-yne.
- **44.** (i) Planar, cyclic, conjugated compounds with $(4n + 2) \pi e^-$ are knows as
 - (ii) Planar, cyclic, conjugated compounds with (4n) πe^- are knows as

3 Mark Questions

45. Convert: Ethylene → Nitrobenzene.

- **46.** Give chemical tests to distinguish the following:
 - (i) Pent-1-yne and pent-2-yne
 - (ii) Ethylene and Acetylene
 - (iii) Ethane and Ethylene
- **47.** Complete the following reactions :
 - (i) CH₃COONa + NaOH →
 - (ii) iso-butyl bromide + alc. KOH →
 - (iii) iso-butyl alcohol + conc. $H_2SO_4 \xrightarrow{\Delta}$

(iv)
$$(CH_3)_2C = CH.CH_3 + HBr \xrightarrow{Peroxide}$$

(v)
$$CH_3$$
— C = $CH_2 + H_2O \xrightarrow{H^+}$
 CH_3

$$(vi) (CH_3)_2 C = CH_2 + Cold dil. KMnO_4 \longrightarrow$$

(vii)
$$(CH_3)_2C = CH.CH_3 + Hot KMnO_4 \longrightarrow$$

(viii)
$$(CH_3)_2C == CH.CH_3 + O_3 \xrightarrow{CH_3COOH} CH_3COOH$$

(ix)
$$CH_3$$
— CH — CH_3 + $\xrightarrow{1. Alc. KOH}$ $\xrightarrow{2. NaNH_2}$ Br Br

$$(x) CaC_2 + H_2O \longrightarrow$$

(xi)
$$CHCl_3 + Ag \longrightarrow$$

(xii)
$$CH_3$$
— $C \equiv CH + H_2O \xrightarrow{H^+} Hg^{2+}$

(xiii)
$$CH_3$$
— $C \equiv CH_2CH_3 + O_3 \xrightarrow{H_2O}$

(xiv)
$$CH_3 - CH = CH_2 + Alc. KMnO_4 \xrightarrow{100^{\circ}C}$$

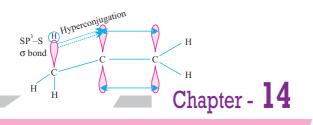
(xv)
$$C_6H_6 + H_2 \xrightarrow{\text{Ni}} 473 \text{ K}$$

- 48. Conversions:
 - (i) Ethane \rightarrow Ethyne
 - (ii) Acetylene \rightarrow But-2-yne

- (iii) Propene → Propanol
- (iv) Acetic acid \rightarrow Methane
- (v) Acetylene \rightarrow Acetone (CH₃COCH₃)
- (vi) Acetylene → Cyclohexane
- **49.** A hydrocarbon (X) on treatment with ammonical AgNO₃ gave white precipitate. On treatment with water in dil. H₂SO₄ and HgSO₄, it gave CH₃—CHO. When (X) is treated with 1mol of NaNH₂/NH₃, along with *n*-propyl bromide, gave compound (Y), which on treatment with Lindlar's catalyst gave (Z) compound (Z) on treatment with O₃ along with Zn gave HCHO and butanal. Identify X, Y, Z and givel all the reactions.
- **50.** An alkyl halide C₅H₁₁Br(A) reacts with alc. KOH to give on alkene (B) which reacts with Br₂ to give compound (C), which on dehydrobromination gives an alkyne (D). On treatment with sodium metal in liquid ammonia, one mole of (D) Give one mole of sodium salt of (D) and half mole of H₂(g). Complete hydrogenation of (D) yields a straight chain alkane. Identify A, B, C and D. Give the reaction involved.
- 51. The sex attractant phormone of codling moth has the molecular formula C₁₃H₂₄O. On catalytic reduction this compound gives 3-Ethyl-7-methyl-1-decanol having molecular formula C₁₃H₂₈O. On reduction ozonolysis the pheromme produces Pentan-2-one, 4-ketohexanal and 2-Hydroxyethanal. On the basis of these information, Write the structure of this pheromme.
- **52.** 896 mL of a hydrocarbon (A) having 87.80% C and 12.19% H weights 3.28 g at STP. Hydrogenation of (A) gives 2-methylpentane. Also compound (A) on hydration in presence of H₂SO₄ and HgSO₄ gives Ketone (B) having molecular formula C₆H₁₂O. The ketone (B) gives a positive iodoform test. Find the structure of (A) give all reactions.

[Hint: (i) 1 mole of a compound at STP contains 22400 mL volume (ii) Ketones having CH₃—C—structures gives positive iodoform test]

- 53. (a) Compound A{C₁₀H₁₈O} undergo reaction with H₂SO₄ at 250°C to yield a mixture of two alkenes {C₁₀H₁₆}. The major alkene product (B) gives only cyclopentanone after ozone treatment followed by reduction with Zn in CH₃COOH. Identify (A) and (B) give the reactions involved.
 - (b) Convert $PhC = CH \longrightarrow PhC = C.CH_3$
 - (c) Benzene does not give addition reactions under normal conditions.



Environmental **Chemistry**

- Environmental chemistry deals with the study of the origin, transport, reactions, effects, fates of chemical species in the environment.
- Environmental pollution is the effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings.
- Main regions of atmosphere are (i) trophosphere (ii) Stratosphere (iii) mesosphere and (iv) ionosphere.
- Pollutants can be (i) gaseous air pollutants (e.g., SO₂, NO₂, CO₂, H₂S, O₃ hydrocarbons etc. and (ii) particular pollutants (e.g., dust, mist, fumes, smoke, smog etc.)
- Gaseous air pollutants: SO₂ can cause acute irritation to the membranes of the eyes resulting in tears and redness. It is also responsible for acid rain.
 NO₂ is extremely toxic to living tissues, textiles and in the production of photochemical smog.
- Particulate pollutants: They are of two types:
 - (i) Visible particulate or viable particulates: There are the minute living organisms that are disposed in atmosphere. Ex. Bacteria, fungi, moulds etc.
 - (ii) Non-viable particulates: These are formed either by the breakdown of larger materials or by the condensation of minute particles and droplets. For example mists, smoke, fumes and dust.
- **Green House Effect** is the phenomenon of warming of earth by absorption and re-emission of solar radiations.
- Green house gases are CO₂, CH₄, O₃ water vapours, chlorofluoro carbons etc.

• Acid raid: When the pH of the rain water drops below 5.6, it is called acid rain. It damages monuments and structures made of firm marble, corrode articles made from metals, destroy plants and trees and it is also harmful to the aquatic life in lakes and rivers.

$$\begin{aligned} &H_2O + SO_2 \longrightarrow H_2SO_3 \\ &SO_2 + O_3 \longrightarrow SO_3 + O_2 \\ &SO_3 + H_2O \longrightarrow H_2SO_4 \\ &NO + O_2 \longrightarrow NO_2 \\ &NO_2 + H_2O \longrightarrow HNO_3 + HNO_2 \end{aligned}$$

- Ozone hole is formed over South Pole due to depletion of ozone layer. CFCs and NO are responsible for ozone layer deplection.
- Effects of deplection of ozone layer: With the depletion of ozone layer, more UV radiation filters into troposphere. UV radiations lead to ageing of skin, cataract, sunburn, skin cancer, killing of many phytoplanktons, damage to fish productivity etc.
- **Smog** is derived from smoke and fog.
- Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and sulphur dioxide. It is also called reducing smog.
- **Photochemical smog** occurs in warm and dry sunny climate. It has high concentration of oxidizing agents and therefore, it is also called as oxidizing smog.
- There are three main components of photochemical smog: nitrogen oxides, ozone and organic derivatives such as acrolein, formaldehyde, peroxyacetyl nitrate (PAN). PAN has the highest toxicity to plants attacking younger leaves and causing 'bronzing' and 'glazing' of their surface.
- Water Pollution: It is mainly caused by industrial waste which include heavy metals like Cd, Pb and Hg.
- **Eutrophication**: The process is which nutrient enriched water bodies support a dense plant population, which kills animal life by depriving

it of oxygen and result in subsequent loss of biodiversity is known as Eutrophication.

- **BOD**: The amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water, is called Biochemical Oxygen Demand (BOD).
- Land Pollution: It is caused by pesticides. Most pesticides can be divided into three categories—Insecticides, Herbicides and fungicides.
- The environmental pollution can be controlled:
 - (a) By recycling of household and industrial wastes.
 - (b) By sewage treatment.
 - (c) Incineration converts organic material to CO₂ and H₂O.
- Green Chemistry is a way of thinking and is about utilizing the existing knowledge and principles of chemistry and other science to reduce the adverse impact on environment.
- Green Chemistry in Day to Day life:
 - (1) Dry cleaning of clothes by using liquified CO₂ along with detergent instead of tetrachloroethene.
 - (2) Bleaching of paper and clothes by using $\rm H_2O_2$ a better bleaching agent as compared to $\rm Cl_2$.
- Global Warming:

About 75% of the solar energy reaching the earth is absorbed by the earth's surface, which increases its temprature, the rest of the heat radiates back to the atmosphere. Some of the heat is trapped by the gases such as CO_2 , CH_4 , O_3 , CFCS and H_2O vapour they add to the heating of the atmosphere causing Global worming.

Environmental chemistry

- 1. Define environmethal pollution.
- 2. Name three toxic metals that can pollute the environment.

- 3. Name the four non-viable particulates present in atmosphere.
- 4. Give one advantage and one disadvantage of ozone in atmosphere.
- 5. What is the name of the compound formed when CO combines with blood?
- **6.** Which gas caused Bhopal Gas Tragedy? Give its formula.
- 7. What is the meaning of the term eutrophication with regard to water pollution?
- **8.** Every year some people die by being in a room containing a faulty heater that uses coal, gas or oil. How might the death occur?
- **9.** Mention two ways to reduce air pollution caused by automobiles.
- **10.** How fluoride in tooth paste protects teeth against decay?

[**Hint**: By converting hydroxyapatite (enamel on the surface of the teeth) into much harder fluorpatite]

- 11. What do you mean by Biochemical oxygen demand (BOD)?
- **12.** Greenhouse effect leads to global warming. Which substances are responsible for greenhouse effect? What does CFC stands for?
- **13.** What does CFC stands for ?
- 14. Which out of CO₂ and CO is more toxic and why?
- **15.** Name the various components into which atmosphere can be divided.

- 1. Write the adverse effect of excessive use of (i) fertilizers, and (ii) pesticides in the soil.
- **2.** Write down the reactions involved during the formation of photochemical smog.
- **3.** Why does rain water normally have a pH of about 5.6? When does it become acid rain? Why is acid rain considered as a threat to Taj Mahal?
- **4.** What are biodegradable and non-biodegradable pollutants?

- **5.** Explain giving reasons "The presence of CO reduce the amount of haemoglobin available in the blood for carrying oxygen to body cells."
- **6.** What should be the tolerable limit of fluoride ions in drinking water? What happens if it is higher than 10 ppm?
- 7. Name four methods for waste management.
- **8.** "Oxygen plays a key role in the troposhere while ozone in the stratosphere." Explain.
- 9. Write the effect of the following gases on human being: SO₂, NO₂, CO, CO₂.
- **10.** What are viable and non-viable particulates?
- 11. How does SO₂ cause pollution? Give steps to control it.
- 12. A person started using underground water after facing acute shortage in municipality water supply. He felt taxative effect. What could be the cause?

- 1. What do you understand by Ozone hole? What are its consequences?
- 2. What do you mean by green chemistry? How will it help decrease environmental pollution?
- 3. How can domestic waste be used as manure?
- **4.** What is the composition of photochemical smog and classical smog? How do the two differ in their behaviour?
- 5. A large no. of fish are suddenly found floating dead on a lake. There is no evidence of toxic dumping but you find an abundance of phytoplankton. Suggest a reason for the fish kill.
- **6.** Do as directed:
 - (i) Name two important sinks of CO₂.
 - (ii) What is marine pollution?

(iii) What is humification?

[Hint: Production of humus by micro-organism in soil]

- 7. In view of green chemistry name the following:
 - (i) A chemical which can be used in place of CFC as blowing agent.
 - (ii) A chemical which can replace chlorine containing bleaching in paper industry.
- **8.** Write the causes of depletion of ozone in the stratosphere. Write reactions also.
- **9.** What are the harmful effects of small size particulate matters?
- **10.** How oxides of nitrogen are generated? What are the harmful effects of oxides of nitrogen?

- 1. What do you understand by greenhouse effect? What are the major greenhouse gases? Why does green house effect leads to global warming? What could be the consequences of globa warming?
- **2.** Discuss the importance of dissolved oxygen in water. What processes are generally responsible for the deoxygenation of the water?
- **3.** How is photochemical smog formed? What are harmful effects of photochemical smog? Give some control measures to reduce photochemical smog?
- 4. What is soil pollutoin? Mention four ways of controlling soil pollution.
- 5. Explain the following terms:
 - (a) Green house effect
 - (b) Green chemistry
 - (c) Ozone layer depletion
 - (d) Global warming
 - (e) Eutrophication

- **6.** (a) Discuss the effects if green house gases were totally missing in earth's atmosphere.
 - (b) Chlorine radicals play an important role in ozone layer depletion. Write chemical reactions in support of the statement.
- 7. For dry cleaning, in the place of tetrachloroethane, liquefied carbon dioxide with suitable detergent is an alternative solvent. What type of harm to the environment will be prevented by stopping use of tetrachloroethane? Will use of liquefied carbon dioxide with detergent by completely safe from the point of view of pollution? Explain.





Solved Practicle Paper - I

Chemisry

Solved Practice Paper-1

Class: XI—Chemistry (Theory)

Time Allowed: 3Hrs M.M.: 70

General Instructions:

- (a) All questions are compulsory.
- (b) Q. No. 1 to 5 are very short answer type questions and carry one mark each.
- (c) Q. No. 6 to 12 are short answer type questions and carry 2 marks each.
- (d) Q. No. 13 to 24 are short answer type questions and carry 3 marks each.
- (f) Q. No. 25 to 27 are long answer type questions and carry 5 marks each.
- 1. Which of the following has maximum number of significant figure? (i) 0.00453 (ii) 4.8046 (iii) 5.643.
- 2. How are 0.5 m NaOH and 0.5 M NaOH different from each other?
- **3.** Explain why Na⁺ is smaller in size than Na atom.
- **4.** Draw resonating structures of CO_3^{2-} ion.
- 5. Define unit cell.
- 6. Determine the emperical formula of an oxide of iron which has 69.9% iron and 30.1% dioxygen by mass. [Atomic mass : Fe = 55.85, O = 16.00]
- 7. (a) Write the electronic configuration of Cu^{2+} ion.
 - (b) Why are Bohr's orbits called stationary states?
- **8.** (a) How many subshells are associated with n = 4?
 - (b) How many electrons will be present in the subshells having m_s value of

$$-\frac{1}{2}$$
 for $n = 4$?

- 9. (a) What do you understand by isoelectronic species?
 - (b) Write a cation and an anion which is isoelectronic with Ar.
- 10. Give the shapes of following covalent molecules using VSEPR theory:
 - (i) NH₃ (ii) ClF₅

Or

- (a) Use molecular orbital theory to product why Be₂ molecule does not exist.
- (b) Compare the stability of O_2^+ and O_2^- .
- 11. Rain damages the monuments like Taj Mahal in Agra when industries are present near by. Why?
- 12. Discuss the relationship between Green house effect and Global warming.
- 13. The work function for caesium atom is 1.9 eV. Calculate.
 - (a) The threshold wavelength.
 - (b) If the caesium element is irradited with a wavelength of 500 nm, calculte the kinetic energy of ejected electron. [Given $1 \text{ eV} = 1.602 \times 10^{-19} \text{J}$]
- **14.** Use the periodic table to identify the following:
 - (a) A group whose elements show valence 2 and 6.
 - (b) A metal which can form a predominantly stable covalent halide of the formula MX.
 - (c) The group having metalloid, non-metal liquid as well as gas at room temperature.
- **15.** Compare the relative stabilities of O₂⁻ & N₂⁺ and comment on their magnetic behaviour.
- **16.** Give reasons for the following:
 - (i) H₂O has higher boiling point than HF.
 - (ii) Ice foats on the surface of water.
 - (iii) KHF₂ exists but KHCl₂ does not.
- 17. What is the hybridisation of the central atom in (i) H₃O⁺, (ii) XeF₂, (iii) XeF₄? What are their geometry?
- **18.** (a) In terms of Charle's law, explain why 273°C is the lowest temperature?
 - (b) 20 mL of hydrogen measured at 15°C are heated to 35°C, what is the new volume at the same pressure.

19. Define van der waal's equation. The van der Waal's constants for two gases are as follows:

Gas	a (atm $L^2 \text{ mol}^{-1}$)	b(L mol ⁻¹)
X	1.39	0.0391
Y	3.59	0.427

Which of them more easily liquefiable and which has greater molecular size?

- **20.** (a) Name the different salts that causes permanent hardness of water. (any two)
 - (b) How do we obtain demineralised water from hard water after passing it from synthetic ion exchange resins? Give reaction?
- **21.** What happen when:
 - (a) Boric acid is added to water.
 - (b) Al is treated with dil. NaOH.
 - (c) BF₃ is treated with NH₃
- **22.** Write IUPAC names of the following:

- (c) Cl
- 23. Write the naming reactions:
 - (i) Wurtz reaction
 - (ii) Decarboxylation of sodium salt of fatty acid
 - (iii) Friedal Craft alkylation reaction.

Or

Complete the following reactions:

(a)
$$CH_3$$
— CH = $CH_2 + HBr$ $\xrightarrow{Peroxide}$?

(b)
$$CH_3$$
— $C1 + Na \xrightarrow{Dry}$?

(c)
$$CH_3$$
— CH — CH_2 — CH_3 $\frac{Alc. KOH}{\Delta}$?

- **24.** (a) Mention two similarities in the behaviour of Be and Al to show that they have diagonal relationship.
 - (b) What is the biological importance of Na in our body?

- **25.** (a) What happens when:
 - (i) Propene is treated with HBr.
 - (ii) Benzene is treated with methyl chloride in the presence of anhydrous. AlCl₃.
 - (iii) When methyl bromide treated with sodium metal in presence of dry ether.
 - (b) Justify that phenolic group in aromatic benzene is ortho and para directing.

Or

- (a) How is benzene obtained from ethyne? What is process called?
- (b) What happens when ethyne is heated with water in the presence of mercuric sulphate and dilute hydrochloric acid?
- (c) What is Markovnikov's Kov rule?
- **26.** (a) Equilibrium constant for a reaction is 10. What will be the equilibrium constant for the reverse reaction?
 - (b) Write the conjugate acids for the Bronsted base OH⁻ and CH₃COO⁻.
 - (c) Determine the pH of 10⁻⁸ MHCl solution taking into account the H⁺ produced by water also. (Given $\log 11 = 1.0414$).
- 27. (a) Propanal and pentan-3-one are the ozonolysis product of an alkene. What is the structural formula of the alkene?
 - (b) An Alkyl halide (A) of formula C₆H₁₃Cl on treatment with alcoholic KOH give two isomeric alkenes (B) and (C)(C_6H_{12}). Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict the structure of A, B and C.

Marking Scheme

- 1. 4.8046.
- 2. In 0.5 m NaOH, 1 mol NaOH present in 1 kg solvent while in 1.0 M NaOH, 1 mol NaOH present in 1 L of solution.
- 3. Na⁺ has only 2 shells and more effective nuclear charge.

5. Correct definition of unit cell

6.

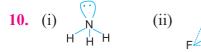
Element	% by mass	At. mass	Relative atoms	Simple Whole number ratio	
Fe	69.9	55.85	$\frac{69.9}{55.85}$ = 1.25	1	2
О	30.1	16.00	$\frac{30.1}{16.00} = 1.88$	1.5	3

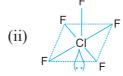
Empirical formula: Fe₂O₃

- **7.** (a) $Cu^{2+}(27)$: [Ar] $3d^94s^\circ$.
 - (b) When an electron is revolving in Bohr's orbit it does not lose energy.
- **8.** (a) n = 4, l = 0, 1, 2, 3

s, p, d, f subshells are associated with n = 4.

- (b) Total number of electrons in shell n = 4 is 32 half of this *i.e.*, 16 elements will have $m_s = -\frac{1}{2}$.
- 9. (a) The species having the same number of electrons are called isoelectronic species.
 - (b) Ca²⁺, Cl⁻





(a) M.O. configuration of Be, molecule is:

$$\sigma 1s^2 \, \sigma^* 1s^2 \, \sigma 2s^2 \, \sigma^* 2s^2$$

Bond order =
$$\frac{1}{2}(4-4) = 0$$

Since bond order is zero, Be, molecule is not possible.

(b) B.O.
$$(O_2^+) = \frac{1}{2}(10 - 5) = 2.5$$

B.O.
$$(O_2^-) = \frac{1}{2}(10 - 7) = 1.5$$

Since B.O. of O_2^+ is more than that of O_2^- , O_2^+ is more stable.

- 11. Industries produce lot of oxides of Nitrogen and Sulphur which dissolve in rain water to form H₂SO₄ and HNO₃. The rain thus becomes acid rain. The marble (CaCO₃) of the monuments is attacked by these acids and get decayed.
- 12. Green house effect traps the incoming radiations of sun. With day by day depletion fo ozone layer. More UV radiations enter the atmosphere. As an effect of the green house, they remain trapped in atmosphere, this leads to rise in temprature of the Earth, which is called Global warming.

13. (a)
$$W_0 = \frac{hc}{\lambda_0}, \lambda_0 = \frac{hc}{W_0}$$

$$\lambda_0 = \frac{6.626 \times 10^{-34} \, \mathrm{J} \, \mathrm{s} \times 3 \times 10^8 \, \, m \, \mathrm{s}^{-1}}{1.9 \times 1.6 \times 10^{-19} \, \mathrm{J}} = 6.538 \times 10^{-7} \, m$$

(b)
$$E = W_0 + K.E.$$

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_0} + \text{K.E.}$$

K.E. =
$$hc \left[\frac{1}{\lambda} - \frac{1}{\lambda_0} \right]$$

= $6.626 \times 10^{-34} \times 3 \times 10^8 \left(\frac{1}{5 \times 10^{-7}} - \frac{1}{6.54 \times 10^{-7}} \right)$

$$= 19.878 \times 10^{-19} \left(\frac{1}{5} - \frac{1}{6.54} \right)$$

$$= 19.88 \times 10^{-19} (0.2 - 0.15)$$

$$= 0.994 \times 10^{-19} \text{ J}$$

- **14.** (a) Group-16
 - (b) Lithium
 - (c) Group-17
- **15.** M.O. electronic configuration of O_2^-

= Bond order =
$$\frac{1}{2}(8-5) = \frac{3}{2} = 1.5$$

M.O. electronic configuration of N₂⁺

Bond order =
$$\frac{1}{2}(7-2) = \frac{5}{2} = 2.5$$

As bond order of N_2^+ > bond order of O_2^- . Therefore, N_2^+ is more stable than O_2^- .

- **16.** (i) Due to strong hydrogen bonding or greater intermolecular hydrogen bonding in H₂O than in H-F. H₂O forms four bond with other water molecule wheres HF forms only two H-bonds.
 - (ii) Density of ice is less than (water) liquid form.
 - (iii) Due to H-bonding in HF H—F.....H—F. This can dissociate to give $\mathrm{HF_2}^-$ ion and hence $\mathrm{KHF_2}$ exists but no H-bonding in H—Cl. So $\mathrm{HCl_2}^-$ ion not exist.
- 17. (i) sp^3 , pyramidal.
 - (ii) sp^3d , linear.
 - (iii) dsp^2 , square planar.
- **18.** (a) At -273 °C, volume of the gas becomes equal to zero *i.e.*, the gas ceases to exist.

(b) According to Charle's law :
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 = 20 \text{ mL } V_2 = ? \text{ mL}$$
 $T_1 = 15 + 273 = 288 \text{ K}$
 $T_2 = 35 + 272 = 308 \text{ K}$
 $V_2 = \frac{V_1 T_2}{T_1} = \frac{20}{288} \times 308 = 21.38$

Volume of hydrogen gas at 35° C = 21.38 mL

19. (a)
$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

- (b) Greater the value of 'a', more easily the gas is liquefiable. Similarly, greater the value 'b' greater is the molecular size. Hence, gas 'y' will be more easily liquefiable and will have greater molecular size.
- **20.** (a) CaCl₂, MgCl₂

(b) In cation exchange resin

$$2RH_{(s)} + M_{(aq)}^{2+} \rightleftharpoons MR_{2(s)} + 2H_{(aq)}^{+}$$

In anion exchange resis

$$RNH_3^+OH^- + X_{(aq)}^- \rightleftharpoons RNH_3^+ X_{(s)}^- + OH^-$$

Finally $H^+ + OH^- \rightleftharpoons H_2O(l)$

- **21.** (i) $B(OH)_3 + 2H_2O \rightarrow B(OH)_4^- + H_3O^+$
 - (ii) $2Al + 2NaOH + 6H_2O \rightarrow 2Na[Al(OH)_4] + 3H_2$
 - (iii) $BF_3 + NH_3 \rightarrow [H_3N \rightarrow BF_3]$ (Adduct)
- 22. IUPAC names of the compounds are:
 - (i) Propylbenzene
 - (ii) 2, 5 Dimethylheptane
 - (iii) 3-Chloropropanal
- 23. (i) Wurtz's reaction:

$$2CH_3Cl + 2Na \xrightarrow{dry \text{ ether}} CH_3 - CH_3 + 2NaCl$$
Ethane

(ii) Decarboxylation of sodium salt of fatty acid with soda line.

RCOONa + NaOH
$$\xrightarrow{\text{CaO}}$$
 R—H + Na₂CO₃

(iii) **Friedal Craft reaction:** When benzene treated with alkyl halide in presence of AlCl₂, Alkyl benzene in formed.

$$+ CH_3C1 \xrightarrow{AlCL_3} + HC1$$

OK

(a)
$$CH_3$$
— $CH = CH_2 + HBr \xrightarrow{Peroxide} CH_3$ — CH_2 — CH_2 — Br

(b)
$$2CH_3Cl + Na \xrightarrow{dry \text{ ether}} CH_3 - CH_3 + 2NaCl$$

(c)
$$CH_3$$
— CH — CH_2 — CH_3 $\xrightarrow{Alc. KOH}$ CH_3 — CH — CH — CH_3
 CI

$$+ CH_3 - CH_2 - CH = CH_2 + KCl + H_2O$$

24. (a) (i) Like Al, Be is not readily attacked by acids because of the presence of an oxide film on the surface metal.

- (ii) $Be(OH)_2$ dissolved in excess of NaOH to give $[Be(OH)_4]^{2-}$ just as $Al(OH)_3$ dissolve in NaOH to form $[Al(OH)_4]^{-1}$.
- (b) Na⁺ ions are present in blood plasma and in the interstitial fluid. These ions participate in the transmission of nerve signals and in regulating the flow of water across cell membranes.

2 – Bromopropane

25. (a) (i)
$$CH_3$$
— CH = CH_2 + HBr \longrightarrow CH_3 — CH — CH_3 | Br

(ii)
$$CH_3$$
 $+ CH_3Cl \xrightarrow{Anhy} + HCl$
 $Towago$

(iii)
$$2CH_3Br + 2Na \xrightarrow{dry} CH_3 - CH_3 + 2NaBr$$

(b) This is because of + R (resonance effect) —OH group. The electron density is increased at *o*- and *p*-positions as compared to at *m*-position. Hence the new group will enter at *p*-position.

Or

(b)
$$HC = CH + HOH \xrightarrow{Hg^{2+}/H^+} [H_2C = CH - OH] \xrightarrow{Tautomerism} CH_3 - C = OH$$

(c)
$$H_2C$$
= CH - CH_3 + HBr \longrightarrow CH_3 - CH - CH_3 $|$ Br

26. (i)
$$K = \frac{1}{10} = 0.1$$

(ii) H₂O, CH₃COOH

(iii) Total
$$[H_3O^+] = [H_3O^+]_{acid} + [H_3O^+]_{H2O}$$

= $10^{-8} + 10^{-7}$
= $11 \times 10^{-8} M$

Н

$$pH = -\log(H_3O^{+)}$$

$$pH = -\log(11 \times 10^{-8})$$

$$pH = -(\log 11 + \log 10^{-8})$$

$$pH = 8 - \log 11$$

$$pH = 8 - 1.0414 = 6.9586$$

27. (a) $CH_3 - CH_2 - CH = C - CH_2 - CH_3$ C_2H_5 3-Ethylhex - 3- ene

Practice Paper-II

Subject: Chemistry (Theory)

Class: XI

Time: 3 Hrs. M.M.: 70

- (i) All questions are compulsory.
- (ii) Q. No. 1 to 5 are Very Short Answer Question carrying 1 mark each.
- (iii)Q. No. 6 to 12 are Short Answer Questions and carrying 2 marks each.
- (iv)Q. No. 13 to 24 are Short Answer Questions and carrying 3 marks each.
- (v) Q. No. 25 to 27 are Long Answer Questions and carrying 5 marks each.
- (vi)Use log tables, if necessary, Use of calculator is not allowed.
- 1. In a reaction $A + B_2 \rightarrow AB_2$, identify the limiting reagent when 2 mole of A are mixed with 3 mole of B_2 .
- 2. Write the general outer electronic configuration of *f*-block elements.
- 3. Define critical temperature.
- **4.** Classify the following as Lewis acid or Lewis base :

- 5. What is the oxidation number of Mn in $KMnO_4$?
- **6.** (a) How many sub-shells are associated with n = 5?
 - (b) How many electrons will be present in these sub-shell having m_s value of $-\frac{1}{2}$ for n = 4?
- **7.** Give one point to differentiate the following thermodynamic terms :
 - (a) Extensive properties and intensive properties.
 - (b) Isothermal process and isobaric process.
- **8.** Account for the following:
 - (a) K₂CO₃ cannot be prepared by Solvay process.
 - (b) Alkali metals are not found in nature in free state.

Or

Write balanced equations for the reaction between:

- (a) Na₂O₂ and water
- (b) Na₂O and CO₂
- **9.** Give suitable reasons for the following:
 - (a) $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ not.
 - (b) Diamond is covalent, yet it has high melting point.

- **10.** (a) What type of isomerism is shown by pentane and 2-methylbutane?
 - (b) Write the name of isomerism among the following compounds:

$$$^{\rm O}_{\parallel}$$$
 $^{\rm CH}_3$ —CH_2—CHO and ${\rm CH}_3$ —C—CH_3

- 11. How green chemistry has helped in the dry cleaning of cloths and laundry?
- 12. What is the impact of use of pesticides on soil pollution?
- 13. Calculate the concentration of nitric acid in moles per litre in a sample which has density 1.40 g mL^{-1} and the mass percent of nitric acid in it being 69%. Molar mass of $\text{HNO}_3 = 63 \text{ g mol}^{-1}$.
- **14.** Account for the following:
 - (a) An anion is always bigger than its parent atom.
 - (b) Chlorine (Cl) have more negative electron gain enthalpy than fluorine (F). [Given: Atomic No. F = 9, Cl = 17]
- 15. Give the shapes of following covalent molecules using VSEPR theory:
 - (a) CIF_3 (b) XeF_4 (c) AsF_5
- **16.** Compare the relative stability of the following species on the basis of molecular orbital theory and indica their magnetic properties:

$$O_2^+, O_2^-, O_2^{2-}$$

- 17. (a) In terms of Charle's law, explain why 273°C is the lowest temperature?
 - (b) Calculate the total pressure in a mixture of 8 g of dioxygen and 4 g of dihydrogen confined in a vess of 1 dm³ at 27°C.

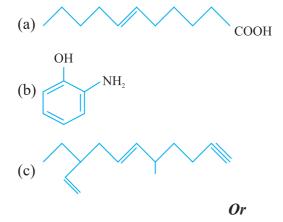
$$[R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}]$$

- **18.** (a) For the reaction, $2Cl(g) \rightarrow Cl_2(g)$, what are the signs of ΔH and ΔS ?
 - (b) For the reaction at 298 K, $2A + B \rightarrow C$, $\Delta H = 400 \text{ kJ mol}^{-1}$ and $\Delta S = 0.2 \text{ kJ}$ K⁻¹ mol⁻¹. At what temperature will the reaction becomes spontaneous?
- **19.** Balance the following redox reaction in basic medium : (Write steps of any one method used)

$$MnO_4^-(aq) + I^-(aq) \rightarrow MnO_2(s) + I_2(s)$$
 [In basic medium]

- **20.** (a) Draw the structure of hydrogen peroxide (H_2O_2) .
 - (b) How do we obtain demineralised water from hard water after passing it from synthetic ion exchange resins? Give reactions.

- **21.** (a) Mention two similarities in the behaviour of Be and Al to show that they have diagonal relationship.
 - (b) What is the biological importance of Na in our body?
- **22.** What happens when:
 - (a) Boric acid is added to water.
 - (b) Al is treated with dil. NaOH.
 - (c) BF₃ is treated with NH₃.
- 23. Write the IUPAC names of the following:



(a) Identify the reagent shown underlined as electrophile or nucleophile : $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

- (b) On complete combustion of 0.246 g of an organic compoundgave 0.198 ga of CO₂ and 0.1014 g of H₂O. Determine the percentage composition of carbon and hydrogen in the compound.
- **24.** Complete the following reactions :

(a)
$$CH_3$$
— CH = CH_2 + HBr ————

(b)
$$C_2H_5$$
— $Cl + Na$ — $Dry ether$

(c)
$$CH_3$$
— CH — CH_2 — CH_3 $\frac{Alc. KOH}{\Delta}$

- 25. (a) Write the electronic configuration of Cr(Z = 24). Why is it differen from the expected configuration?
 - (b) The mass of an electron is 9.1×10^{-31} kg and its kinectic energy is 3×10^{-25} J. Calculate its wavelength.

(c) Which of the following orbitals is not possible and why?

Or

- (a) Calculate the wavelength and frequency of limiting line of Lyman series (Rydberg constant = 109677 cm⁻¹).
- (b) Give quantum numbers for electrons with highest energy in sodium atom (Atomic number of sodium = 11).
- (c) Which of the following sets of quantum number are not possible? Give reasons:

(i)
$$n = 1$$
, $l = 0$, $m_l = 0$, $m_s = -\frac{1}{2}$

(ii)
$$n = 2$$
, $l = 0$, $m_l = 0$, $m_s = 0$

- **26.** (a) Equilibrium constant for a reaction is 10. What will be the equilibrium constant for the reverse reaction?
 - (b) Write the conjugate acids for the Bronsted base OH⁻ and CH₃COO⁻.
 - (c) Determine the pH of 10^{-8} M HCl solution taking into account the H⁺ produced by water also. (Given: log 11 = 1.0414)

Or

(a) At certain temperature and total pressure of 10⁵ Pa, iodine vapour contains 40% by volume of I atoms :

$$I_2(g) \rightleftharpoons 2I(g)$$

Calculate K_n for the equlibrium.

- (b) What is the effect of:
 - (i) Addition of H₂
 - (ii) Removal of CO

on the equilibrium :
$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$

- (c) Mention one application of solubility product.
- **27.** (a) Propanal and pentan-3-one are the ozonolysis product of an alkene. What is the structural formul of the alkene?

(b) Give the main products of the reactions:

$$(i) + CH_3COC1 \xrightarrow{Anhy. AlCl_3}$$

(ii)
$$CH_3 - C = CH_2 + H_2O \xrightarrow{H^+} CH_3$$

(iii)
$$+ \text{Cl}_2 \xrightarrow{h\upsilon}$$
?

- (a) An alkyl halide (A) of formula $C_6H_{13}Cl$ on treatment with alcoholic KOH give two isomeric alkenes (B) and (C) (C_6H_{12}). Both alkenes on hydrogenation give 2, 3-Dimethylbutane. Predict the structure of A, B and C.
- (b) Why does benzene show electrophilic substitution easily?
- (c) Name the compound that will be required to obtain butane using Kolbe's electrolysis process.

Practice Paper-III

Subject: Chemistry (Theory)

Class: XI

Time: 3 Hrs. M.M.: 70

- (i) All questions are compulsory.
- (ii) Q. No. 1 to 5 are Very Short Answer Question carrying 1 mark each.
- (iii)Q. No. 6 to 12 are Short Answer Questions and carrying 2 marks each.
- (iv)Q. No. 13 to 24 are Short Answer Questions and carrying 3 marks each.
- (v) Q. No. 25 to 27 are Long Answer Questions and carrying 5 marks each.
- (vi)Use log tables, if necessary, Use of calculator is not allowed.
- 1. Define electron gain enthalpy.
- 2. In which orbital will the electrons enter first 3d or 4p?
- **3.** Write I.U.P.A.C. name of the following compound:

- 4. Define standad enthalpy of formation.
- 5. Write electronic configuration of Cu^{2+} ion. (Atomic number of Cu = 29).
- 6. How does Heisenberg's uncertanity principle support concept of orbital?
- 7. Give the units of vander waal's constants. Also point out their significance.
- **8.** 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in carius estimation. Calculate the percentage of chlorine present in compound.
- **9.** Write the short notes on:
 - (a) Wurtz Reaction (b) Freidal Craft's Alkylation
- **10.** Write the molecular shapes of :

(a) XeF_4 (b) CIF_3

- 11. Determine the emperical formula of an oxide of iron which has 69.9% iron and 30.1% dioxygen by man. [Atomic mass: Fe = 55.85, O = 16.00]
- **12.** The ionization enthalpy of lithium is 520 kJmol⁻¹, calculate the amount of energy required to convert 140 mg of lithium atoms in gaseous state into Li⁺ ion.
- **13.** Compelete the following reactions:

(a) $CH_3 - CH = CH_2 + HBr \xrightarrow{peroxide}$

(b)
$$CH_3 - Cl + Na \xrightarrow{Dry}$$

(c)
$$CH_3 - CH - CH_2 - CH_3 \xrightarrow{\text{alc. KOH}} \Delta$$

$$C1$$

14. Balance the following reaction in acidic medium:

$$MnO_4^-(aq) + SO_2(g) \longrightarrow Mn^{2+}(aq) + HSO_4^-(aq)$$

- **15.** The value of K_C for the reaction:
 - $2A \rightleftharpoons B + C$ is 2×10^{-3} at 500K. At given time, the composition of reaction mixture is $[A] = [B] = [C] = 3 \times 10^{-4}$ M. Is the reaction mixture at equilibrium? If not, what is the direction of net reaction?
- **16.** (i) Write down the nature of below reaction with reason:
 - (a) $NH_3 + H^+ \rightarrow NH_4^+$
 - (b) $BF_3 + NH_3 \rightarrow F_3B \leftarrow NH_3$
 - (c) $H_2SO_4 \rightarrow H^+ + HSO_4^-$
- 17. (i) Arrange the following carbocation in creasing order of their stability. (CH₃)₂CH⁺,CH₃CH⁺₂,(CH₃)₃C⁺,CH⁺₃
- 18. How will you convert
 - (a) Propan-1-ol into propene
 - (b) 2-bromopropane into But-2-ene
 - (c) Ethyl amine into ethyl isocyanide
- 19. (i) Define eutrophication and penumocanosis.
 - (ii) Write difference in between photochemical and classical smog.
- **20.** (i) Calculate the oxidation number of S in $S_2O_6^{-2}$ having $(-O-O-)^{2-1}$ linkage and C in CH₃COOH.
 - (ii) Balance the equation in basic medium by half reaction method $P_4(s) \rightarrow PH_3(g) + H_2PO_2^-(Aq)$
- **21.** (a) Out of staggerd and eclipsed conformations of n-butane, which is more stable and why?
 - (b) What causes the temporary and permanent hardness of water.
- **22.** Write a breif note on the following environmental terms:
 - (a) Acid rains
 - (b) Eutrophication/Green House effect
 - (c) Green chemistry
- 23. (a) Define buffer solution.
 - (b) The solubility of Sr(OH)₂ at 298 K is 19.23g/L of solution. Calculate the concentration of strontium and hydroxyl ions and the pH of the solution.

- **24.** Write any three main biological importance of Ca and Mg.
- **25.** (i) The stability of peroxide and superoxide of alkali metals increases as we go down the group. Explain giving reasons.
 - (ii) How to control photochemical smog.

OR

- (i) Derive first law of thermodynamics.
- (ii) Define enthalpy of neutralisation.
- (iii) Calculate the ΔH^{θ} of the reaction.

$$\begin{array}{c}
H \\
| \\
H - C - Cl(g) \longrightarrow 1C + 3H + 1Cl \\
| \\
H
\end{array}$$

Bone enthalpies of C-H & C-Cl bond are 415 kJ mol⁻¹ & 326 kJ mol⁻¹

- **26.** (a) Account for the following:
 - (i) Boron Halides do not dimerise like BH₃.
 - (ii) Carbon shows catenation
 - (iii) PbCl₄ is a good oxidising agent.
 - (b) Complete the following reactions:
 - (i) $B_2H_6 + 3O_2 \longrightarrow$
 - (ii) $2BF_3 + 6 NaH \xrightarrow{450 K}$

OR

- (a) Write equation to justify amphoteric nature of Water.
- (b) What is application of equilibrium constant.
- (c) What are the full form of BOD?
- 27. (a) Is the entropy of the universe constant?
 - (b) If standard free energy change for a reaction is found to be zero, what is its equilibrium constant.
 - (c) Define common ion effect.

OR

- (a) Calculate the degree of ionisation of 0.1 mol/L solution of acetic acid, given K_a for CH₃COOH 1.8 \times 10⁻⁵ mol/L
- (b) Define the following terms:
- (i) Solubility product
- (ii) Buffer solution
- (iii) Henderson equation

Practice Paper-IV

Subject: Chemistry (Theory)

Class: XI

Time: 3 Hrs. M.M.: 70

- (i) All questions are compulsory.
- (ii) Q. No. 1 to 5 are Very Short Answer Question carrying 1 mark each.
- (iii)Q. No. 6 to 12 are Short Answer Questions and carrying 2 marks each.
- (iv)Q. No. 13 to 24 are Short Answer Questions and carrying 3 marks each.
- (v) Q. No. 25 to 27 are Long Answer Questions and carrying 5 marks each.
- (vi)Use log tables, if necessary, Use of calculator is not allowed.
- 1. Define critical temperature.
- 2. What is the oxidation number of Mn in KMnO₄?
- 3. Write the electronic configuration of Cr^{3+} ?
- 4. Write the IUPAC name of an element having atomic number 105?
- **5.** State Boyle's law?
- **6.** (a) What is redox reaction?
 - (b) Identify the substance reduced in the following reaction.

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$$

- **7.** Explain why?
 - (a) Cs is used in photoelectric cell.
 - (b) Potassium carbonate cannot be prepared by solvey process.
- 8. (a) State Pauli's exclusion principle.
 - (b) What is the lowest value of 'n' that allows 'g' orbital to exist.
- 9. (a) Find the [H+] ion concentration in 100 mL of 0.001 M NaOH solution.
 - (b) Write the nature of following solution.

(i)
$$[OH^-] = 10^{-5}$$

(ii)
$$[OH^-] = 10^{-10}$$

10. Write the name and number of the each type of the bonds in the following compound.



- 11. Write balanced equations for the equation between.
 - (a) Na₂O₂ and water
 - (b) Na₂O and CO₂
- 12. (a) What type of isomerism is shown by pentane and 2-methylbutane?
 - (b) Write the name of isomerism among the following compound.

$$\mathrm{CH_3-CH_2-CHO}$$
 and $\mathrm{CH_3-C-CH_3}$ \parallel O

- 13. Write the name reactions:
 - (i) Wurtz reaction
 - (ii) Decarboxylation
 - (iii) Kolbe's Electrolysis
- **14.** Compare the relative stabilities of O_2^- and N_2^+ and comment on their magnetic behaviour.
- **15.** (a) Find oxidation number of
 - (i) Mn in MnO₄-
- (ii) O in H₂O₂
- (b Balance the following equation by ion electron method in basic medium

$$MnO_4^- + I^- \longrightarrow MnO_2 + IO_3^-$$

- **16.** Give the reasons for the following:
 - (a) Electron gain enthalpy of fluorine is less negative that of chlorine.
 - (b) Anionic radius is always more than that of oxygen.
 - (c) Ionization ethlapy of nitrogen is more than that of oxygen.
- 17. A neon-dioxygen mixture contains 70.6g dioxygen and 167.5g neon. If pressure of the mixture of gases in the cylinder is 25 bar. What is the partial pressure of dioxygen and neon in the mixture.

- **18.** (i) XeF₄ has AB₄E₂ type molecule draw the arrangement of electron pair.
 - (ii) Discus the shape (geomatry) of NH₃ or H₂O on the basis of hydridization.
- 19. (a) Explain electrophile and nucleaphile with one example each.
 - (b) Write the possible Tautomer of the acetone (CH₃ CO CH₃).
 - (c) Explain the Inductive effect.
- **20.** (a) How is diborane prepared in the laboratory? Draw its structure.
 - (b) Explain why CO is a gas whereas SiO₂ is a solid.
 - (c) Write the shape of PCl₅.
- **21.** Write the IUPAC names of the following:

(c)

22. (a) Identify the reagent shown underlined as electrophile or nucleophile :

$$CH_3COOH + OH \longrightarrow CH_3COO + H_2O$$

- (b) On complete combustion of 0.246 g of an organic compound gave 0.198g of CO₂ and 0.1014 g of H₂O. Determine the percentage composition of carbon and hydrogen in the compound.
- **23.** (a) Calculate the total pressure in a mixture of 8 g of dioxygen and 4 g of dihydrogen confined in a vessel of 1 dm³ at 27°C.

[Given
$$R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$$
]

- (b) Critical tempreature of CO_2 and CH_4 are 31.1°C and 81.9°C respectively. Which of these has strongen intermolecular forces and why?
- **24.** How can you apply green chemistry for the following:
 - (i) to control photochemical smog.

- (ii) to reduce used of synthetic detergents.
- (iii) to reduce the consumption of petrol and diesel.
- 25. (a) Explain the following with example
 - (i) Common ion effect
 - (ii) Buffer solution
 - (b) At a certain tempreature and total pressure of 10^5 pa, iodine vapour contains 40% by volume of I atoms

$$I_2(g) \Longrightarrow 2I(g)$$

Calculate K_n for the equilibrium.

OR

- (a) Define Le-Chateler's principle.
- (b) Define pH.
- (c) Equilibrium constant for the reaction is 4.0. What will be the equilibrium constant for the reverse reaction.
- (d) Calculate the pH of 10^{-3} M NaOH solution.
- **26.** (a) Define Heisenberg's uncertainty principle. Write its Mathematical exopression.
 - (b) Calculate the uncertainity in the velocity of a cricket ball of mass 150 g. If the uncertainity in its position is of the order of 1° A.

$$(h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{s}^{-1})$$

OR

- (a) Which of the following orbitals are not possible? 1p, 2s, 2p, 3s
- (b) Which of the following sets of quantum number are not possible? Give reason:

(i)
$$n = 0$$
, $l = 0$, $m_l = 0$ $m_s = +\frac{1}{2}$

(ii)
$$n = 1, 1 = 0, m_l = 0 m_s = -\frac{1}{2}$$

(c) Electron are emitted with zero velocity from a metal surface when it is expressed to radiation of wavelength 6800 Å. Calculate threshold frequency (v_0) and work function (W_0) of the metal.

27. (a) Define the following with example:

- (i) Antimarkovnikev's addition
- (ii) Morkovnikoff's Rule
- (b) Give the main product of the reaction:

(i)
$$+ CH_3 - Cl \xrightarrow{Anhyd AlCl_3}$$

(ii)
$$+ HNO_3 \xrightarrow{\text{conc } H_2SO_4} \rightarrow$$

(ii)
$$CH_3 - C = CH_2 + H_2O \xrightarrow{\Delta}$$

OR

- (a) How can you convert the following:
 - (i) Propane-1-ol to propan-2-ol
 - (ii) Ethyl chloride to n-Butane.
- (b) Complete the following reaction:

(i)
$$CH_3 - CH = CH_2 + HBr$$
 Organic peroxide \rightarrow

(ii)
$$CH_3$$
— $Cl + Na$ — Ory ether

(iii)
$$CH_3$$
— $CH = CH_2$ — CH_3 $\xrightarrow{alc KOH} \Delta$

NOTE